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A LABORATORY OUTLINE OF GENERAL CHEMISTRY

BY

ALEXANDER SMITH

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COLUMBIA UNIVERSITY

Fourth Edition.

REVISED IN COLLABORATION WITH

WILLIAM J. HALE

ASSISTANT PROFESSOR OF CHEMISTRY IN THE
UNIVERSITY OF MICHIGAN

*FORTY-SECOND
THOUSAND*

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PREFACE TO THE THIRD EDITION

The extensive use of the previous editions seems to have shown the acceptability of the general plan of the book. This conclusion has been confirmed by the fact that the second edition has been translated into German, and that a translation of the present one into Russian is being prepared. In the present, therefore, the fundamental features of the previous edition have been preserved. In brief, the aim has been to furnish the basis for a systematic, coherent, and instructive study of the elements of chemistry from the modern standpoint.

In the effort to make misapprehensions and mistakes as nearly impossible as may be, the directions have been entirely rewritten, and in many cases have been amplified, and a number of the experiments have been modified. An entirely new set of figures has also been drawn. To render the exercises more instructive, and still further to discourage mechanical work, a larger number of questions has been inserted. With the same end in view, data in regard to solubility have been introduced (Appendix) as a new feature, and their use in explaining chemical phenomena has been illustrated in many experiments. The rationalizing value of using the conceptions of chemical dynamics, the electromotive series, and the degrees of ionization has been emphasized by more frequent references.

Some of the formal quantitative experiments have been modified, and the directions have been made clearer. The value of these experiments has been found to lie chiefly in the basis they give for clear understanding of the difficult subject of combining, atomic, and molecular weights.

When quantitative experiments were first used in elementary chemistry it was hoped that they would also assist in developing an abiding realization of the quantitativeness of all chemical phenomena and, as a consequence, make all the thought and work of the student more rigorous. In the experience of the authors, however, quantitative experiments of the usual kind fail to accomplish this important result. Students who have performed such experiments still add a test-tube full of sulphuric acid to a liquid known to contain only a trace of a compound of lead, and still think less than a dozen bubbles of hydrogen sulphide sufficient to precipitate the lead from

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10 cc. of approximately normal lead nitrate solution (see **74** *g* and note 36, p. 67). They attempt to make potassium chlorate without considering that a few bubbles of chlorine (perhaps liberally mixed with air) will not saturate three grams of potassium hydroxide (see **57** *a*), or they take too much water and then, not having considered the solubilities and, therefore, not knowing what is wrong, throw away the product and lose valuable time by starting entirely *ab initio*. The failures which result from this lack of a sense of quantity are innumerable, and the discouragement often a serious hindrance to ultimate success. The fault, of course, is in the instruction, and the remedy lies in exercises and questions devised to cultivate **this** missing sense. It is to meet this situation that the tables of solubilities have been introduced and have been referred to frequently (see, *e.g.*, **54**, **55**, **126** *a*, **127**, **137** *c–f*, **139** *d*). With the same object, the tables of degrees of ionization have been utilized (see *e.g.*, **64**, **66**), and the varying degrees of activity of acids have been observed (*e.g.*, **154**) and measured (**120**). Still further to cultivate rational experimentation, the solutions on the side-shelf should be approximately normal (or in simple multiples or submultiples of this concentration), and the student may then be led to note the concentrations and, in many experiments, to take suitable quantities accordingly. The importance of the point of view indicated in the foregoing can hardly be overestimated. Genuine success in business or in the professions, and often even the mere making of a livelihood, depend so largely on ability to reason quantitatively that practice in this kind of reasoning is of inestimable value in education. If, on the contrary, the work in chemistry is purely haphazard in this respect, the study of the science may easily be a positive detriment rather than a benefit, and that whether the student ultimately makes direct use of his knowledge of the science or not.

If it appears that these changes have made the work more difficult, it must be remembered that valuable knowledge can be obtained only by effort, and that the value of the knowledge is in proportion to the effort, provided the latter is directed rationally along instructive lines. Easy chemistry must be superficial and empirical, in proportion to its simplicity. It is easy to perform experiments mechanically; it is necessarily more difficult to interpret the results and extract all that they can teach.

The book is intended for beginners in colleges, universities, and professional schools. It must be understood, however, that no one class is expected to perform all the experiments.

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Only from one-half to three-quarters of the whole material can be covered in thirty-three weeks, by a student working four to six hours a week. The authors have found no difficulty in arranging a course only twelve weeks long, and utilizing considerably less than half the contents. The outline is subdivided into numerous small paragraphs, so that each instructor may be able to make such a selection as will suit the work he desires to give. It is hoped that the whole body of material is sufficiently great to permit the arrangement of a course of almost any character. Thus, many or few quantitative experiments may be given, and many or few theoretical matters illustrated. Emphasis may be laid on work leading to analysis, or some of that work may be sacrificed in order to include a larger number of preparations. The student may even be directed in certain paragraphs to ignore the questions. Finally, the order of the experiments may be altered without serious disturbance.

The recent great improvement in the work in chemistry in secondary schools makes it desirable to recognize and encourage this work by outlining a different selection of experiments for those who have studied the science before, and, if possible, to give such students separate class-room instruction.

Sample selections of experiments for beginners and for more advanced students have been given in a separate pamphlet, which will be sent to instructors, upon request, by publishers. This pamphlet includes also lists of apparatus and chemicals and other data helpful in the organization of the laboratory instruction.

In the preparation of this edition the authors have received helpful suggestions from Prof. S. Lawrence Bigelow of the University of Michigan, from Prof. Ralph H. McKee of Lake Forest University, and from Prof. H. N. McCoy, Dr. C. M. Carson, and Mr. T. B. Freas of the University of Chicago, as well as from many others. We wish here gratefully to acknowledge the improvements which the *Outline* owes to these suggestions.

THE AUTHORS.

CHICAGO AND ANN ARBOR,
May, 1907

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PREFACE TO THE FOURTH EDITION

The third revised edition having been exhausted within a few months of its publication, the opportunity is taken to introduce some needed alterations. Aside from a few corrections, only one considerable change is made. This consists in the transfer of Chapter V of the last edition bodily so that it follows Chapter VII of the same edition. This places the quantitative experiments on equivalent weights after the work on water, chlorine and hydrogen chloride instead of before it. In the "Introduction to General Inorganic Chemistry," to which the Outline is a companion volume, the discussions of molecular and atomic weights and of the atomic hypothesis occur at this point and are therefore now contemporaneous with the quantitative experiments dealing in part with the same subjects. Thus there have been adjusted the two difficulties in making a convenient scheme of work, which were formerly occasioned by the lack of laboratory work to accompany the molecular and atomic hypotheses and their applications, and, at a different stage, the great excess of laboratory work over class-room work at the time when the main set of quantitative experiments was being performed. Many instructors will feel that, apart from this mere matter of pedagogical convenience, the postponement of the quantitative work is in itself advantageous, because, after more laboratory experience, greater ease of performance and greater accuracy in results may now reasonably be expected.

This opportunity may be taken to call attention to the change in the nomenclature of ionic substances (p. 55) in Chapter X *et seq.* This considerable departure from the system used in the text-book was made only after careful consideration. The nomenclature now employed in the outline, although it has been developed chiefly since the text-book was written, has already come into fairly consistent use in American chemical literature. In Great Britain no one system has established itself. In Germany a plan similar to that here adopted has been used by Ostwald and others for several years.

THE AUTHORS.

November, 1907.

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GENERAL INSTRUCTIONS.

NOTES 1–17.

Read the "Regulations" posted in the laboratory. **Read also,** attentively, the following notes:

Note 1. — Provide yourself with a **note-book** and make a careful permanent record immediately after each experiment. Enter the numbers and titles of the paragraphs of the outline systematically. State (1) what you did, if anything beyond the directions, but do not copy the printed directions themselves, (2) what you observed, (3) what conclusions you drew. A sketch of the apparatus will enable you to recall the circumstances of the experiment, if later reference to it is necessary. This note-book, when called for, is to be handed in for inspection.

The **blank pages** in this *Outline* are not intended for the final notes. They may be used for individual suggestions given by the instructor, preliminary notes, record of weighings, etc.

The directions have been expressed with the utmost care and brevity. Every word is significant. Italics are therefore nowhere employed for the purpose of emphasis.

Note 2. — Whenever an **interrogation point** or a direct **question** appears a corresponding note should appear in the note-book. The "(?)" indicates something to be observed and recorded.

Note 3. — The very numerous **questions** asked in the course of this outline are intended to be answered, not by speculation, but by careful observation and reasoning based on the results of this. Very often the student will find it necessary to devise and carry out further experiments of his own before a satisfactory answer is obtained. When a question occurs to you, endeavor by reflection and study to answer it yourself before consulting an instructor.

Note 4. — In many cases the work outlined could not in itself furnish the basis for an answer, and fuller investigation of the point would require work beyond the time or ability at the disposal of the beginner. Such questions are distinguished by an [R], indicating that Reference to some authority (lecture, book, or assistant) must be made. The number following the R is that of the page in Alexander Smith's *Introduction to General Inorganic Chemistry*, where the necessary information may be obtained. The authority should be consulted, however, only after the experiments have been made and the notes written up as far as possible.

Note 5. — When a chemical change has been observed the **equation** should always be given in the notes, but an equation alone is never a sufficient record.

Note 6. — Where the word [Instructions] appears, consult the instructor before going further.

Note 7. — In quantitative experiments, marked [Quant.], use the finer balance, in all other cases the rough scales in the laboratory.

Note 8. — The expression [Storeroom] indicates that the necessary apparatus is not included in the individual outfits.

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Note 9. — When the word [Hood] appears, the operation is not to be conducted at the desk in the open laboratory. The apparatus is to be at once transferred to the hood provided for operations involving ill-smelling gases or vapors.

Note 10. — Where exact quantities are not indicated, very small amounts of solutions (1 c.c. or less) should be taken. This advice is given, partly to secure saving of material, but chiefly to avoid the waste of time which working with large quantities always entails.

Note 11. — To **obtain the necessary chemical substances**, do not carry the bottles from the side-shelf to the desk. Bring a clean test-tube for liquids and a watch-glass for solids. For the latter, a piece of the paper, provided near the side-shelf, may also be used. When too much of any reagent has been taken, do not return it to the bottle.

Note 12. — The **chemicals** are divided into two sets, each arranged alphabetically according to the scientific names.* The first set consists of solids in small bottles, the second of liquids. The bottles and their places are numbered consecutively to facilitate accurate replacement, and scrupulous care must be taken not to disarrange them. Read the labels attentively, as there are frequently several kinds of the same substance (*e.g.*, pure, and commercial, dilute, concentrated, and normal).

All **materials** are supplied through the storeroom service. Do not therefore take side-shelf bottles, when found **empty**, to the instructor, but to the storekeeper for refilling.

Note 13. — The expression [From Instructor], however, indicates one of a few special substances for which the student must apply to an instructor.

Note 14. — The **nine bottles on the desk** contain aqueous solutions of sodium hydroxide, sodium carbonate, and ammonium hydroxide, which are not to be found on the side-shelves, and sulphuric, hydrochloric, and nitric acids in concentrated and dilute form. These acids are all commercial. The corresponding *pure* concentrated and dilute acids will be found on the side-shelf, but are to be used only when the outline so directs.

Note 15. — When any **acid gets upon the clothing**, apply ammonium hydroxide solution [On desk] at once.

Note 16. — **Burns**, whether caused by contact with hot objects, by acids, or by corrosive liquids like bromine, are rubbed gently with a paste of sodium-hydrogen carbonate and water. All burns, save the slightest, must afterwards be dressed with an aqueous solution of boric acid (half-saturated) [Side-shelf] to prevent infection. Obtain the assistance of an instructor.

Cuts must be washed in running water and dressed with boric acid as above, or with lanolin containing 2 per cent of boric acid.

Note 17. — All students **work independently**, except where coöperation of two students is expressly directed.

* A pamphlet containing lists of the chemicals and apparatus required will be furnished, on application, by the publishers.

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LABORATORY OUTLINE

CHAPTER I.

MANIPULATION.

1. The Outfit of Apparatus. As articles missing or found imperfect when the course is completed will be charged for, check the outfit of apparatus carefully by comparison with the list. To do this, put all the articles on the top of the desk and make a mark on the margin of the list opposite to the names of such as you are able to identify, at the same time returning the article to the cupboard or drawer. With the assistance of an instructor, the remaining, unfamiliar articles can then be checked also.

2. Instructions.

a. Read the general instructions and notes preceding this chapter very carefully, and do not fail to observe them.

b. The number of blast-lamps and balances being limited, the whole class cannot perform the experiments in this chapter simultaneously in the order given. The order is, in any case, a matter of indifference. Two students from the group under each assistant will begin with glass-working (**4**) or weighing (**6** and **7** *a* and *b*). The other students will meanwhile perform **3**, **5**, and **7** *d* at the desks.

c. Record in the note-book the results of **3**, **6**, and **7** only.

3. Bunsen Burner.

a. Attach the Bunsen burner by means of rubber tubing to a gas connection, close the air-holes at the base, and light. Now open the air-holes gradually and note the effect upon the flame (?). What is the proximate cause of the difference in the two flames? When using the burner for heating purposes, always regulate the air supply so as to get a noiseless, non-luminous flame.

b. Determine the structure of each kind of flame. Which parts are relatively hotter, and which cooler? This may be ascertained by observing the quality of the glow produced in a platinum wire held across the flame in several positions. A match-stick quickly inserted may also indicate the cooler portions. Make sketches showing the real form of the flame (?). Where should you hold an object in the non-luminous flame, in order

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to get the greatest heating effect? Prove the presence of unburnt gas in the inner cone by inserting therein one end of a narrow glass tube, and igniting the gas that issues from its upper end. Which region is deficient in oxygen and which has an excess? The former is called the reducing, the latter the oxidizing region.

c. Bring from the side-shelf, in a watch-glass [Note 12, p. 2], a small quantity of borax* (sodium tetraborate). Heat your platinum wire, which has been inserted into the fused end of a glass rod, and immerse the glowing end of the wire in the borax. Use the wire in straight condition, without any loop. Now, hold the wire in the flame, observe the behavior of the borax, and explain [R 528. See Note 4, p. 1]. The bead must be small to avoid its dropping off.

d. Bring the hot borax bead in contact with a minute particle of manganese dioxide [Notes 11 and 12], heat in the flame near the outer edge until the particle has dissolved, and observe the color of the bead when cold. If the bead is opaque, too much of the dioxide has been taken: throw the molten bead off and start again.

e. Cut off the gas supply until the flame is about 6 cm. in height. Close the air-holes until a luminous point appears at the apex of the inner cone, and hold the bead containing the manganese dioxide steadily in this luminous (reducing) portion. Before withdrawing the bead, lower it into the inner cone of unburnt gases to cool. Observe the color of the bead (?).

f. Reheat the bead in the oxidizing part of the flame (?).

4. Glass-Working [Blast-Lamp Table. Instructions, and Note 18, below].

a. Cut a small piece off the wide soft glass tubing and make a test-tube out of it.

b. Make a test-tube of hard (? [R 607]) glass.

c. Connect two pieces of narrow glass tubing to make a longer piece.

d. Make a T-tube by connecting two pieces of narrow glass tubing at right angles to each other.

Note 18. — To **cut narrow glass tubing** make a slight, transverse scratch with the triangular file. Hold the tubing so that the points of the thumbs are together opposite to the scratch, and press forward with the thumbs so as to bend the tube away from this mark. Wide tubing may be cut by making a deep scratch completely round the tube and starting the crack by touching with

* In this *Outline* the common, or popular names are often used intentionally. The systematic names must, in such cases, be found by the student [R].

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the red-hot end of a glass rod. Other methods may be shown by the instructor.

Always round off (**fire-polish**) the sharp edges of freshly cut tubes by softening in the Bunsen flame (why do the edges become rounded?). In the case of test-tubes, and other tubes of wide bore in which corks are to be inserted, the mouth must be strengthened and rendered fit for receiving the cork. To accomplish this, heat the edge in the flame and spread it slightly, but uniformly, by rotating in it a pointed piece of charcoal, or by turning outward the softened edge with the reverse end of a file.

In making test-tubes and in connecting pieces of tubing, distend the softened parts by blowing immediately before allowing to cool, otherwise cracks are likely to appear.

To **bend glass tubing**, never use the Bunsen flame (why? Note 3). Always employ an ordinary, flat, luminous flame of fish-tail form. Hold the tubing lengthwise in the flame, not across it (why?), turning the tube slowly round its axis to receive uniform heating. Keep the tube straight until it is soft enough to bend by its own weight. Finally, do not actually make the bend while the tube is in the flame, but after removal from it (why?).

Hold a piece of tubing in the Bunsen flame, without rotating the tube, and bend it while it is in the flame (?). Compare the bend with one made in the proper way and account for the difference.

5. Construction of a Wash-Bottle. Select a good cork which will fit the mouth of the largest flask and soften it by rolling under the foot upon the floor while pressure is cautiously applied. Bore two parallel holes with the cork-borer, and smooth them by means of a rat-tail file [Note 19, below]. Bend two pieces of glass tubing as indicated in Fig. 1 [Note 18], fire-polish their edges and insert them in the openings in the cork. Make the nozzle by softening a piece of glass tubing in the Bunsen flame, drawing it to capillary dimensions after removal from the flame, cutting (6–8 cm. long), and fire-polishing. Connect the nozzle by means of a short piece of rubber tubing. Test the apparatus to see that it is air-tight [Note 20]. Finally, fill the flask with distilled water [Note 21].

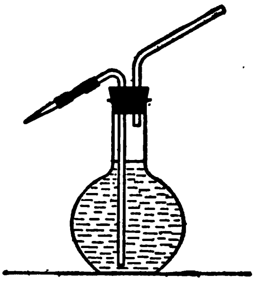

Fig. 1

Note 19. — The **cork borer** is usually made of brass, and the edge is easily turned. Form the habit of examining the edge and freshening it by cautious application of a triangular file [Instructions. Note 6] every time it is to be used. Do not hold the cork

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against the table while boring, as the edge of the tool may be ruined. Hold the cork in the hand and bore from the narrow end with care, exactly parallel to the axis. If the cork and borer are rotated round their axes and the edge is fresh, very little force will be required. The borer is purposely chosen so as to be smaller than the tubing. Its use thus permits the enlarging and smoothing of the hole with the rat-tail file until a perfectly fitting bore has been made.

Note 20. — Before use, every piece of closed apparatus employed in this and all succeeding experiments must be **tested for air-tightness**, and rendered perfectly air-tight. In this instance place in the flask enough water to cover the lower end of the longer tube and transfer the rubber connection to the shorter glass tube and close it with a clamp. Now, blow through the longer tube so that a few bubbles of air pass into the flask. If the apparatus is air-tight the water will rise in this tube when the mouth is withdrawn and will remain in an elevated position. If the water gradually sinks to its former level, the apparatus is not air-tight. Examination of the holes in the cork may show defects, which can be remedied only by boring a fresh cork more carefully. If the cork itself contains pores, these may often be closed by thorough wetting. Do not on any account employ paraffin or sealing-wax to patch defective places in a cork; use a fresh one.

Note 21. — **Distilled water** is to be used for making solutions and for rinsing glassware (why?). Common water is to be used for all other purposes.

6. Use of the Simple Balance [Instructions. Quant.]. By turning the screw attachment in front of balance case, release the beam and pans, allowing the beam to swing. Observe the excursions made by the pointer. Divide by two the total divisions covered by the pointer in one full swing, and count off from either end of the swing the divisions which this number designates, thus finding the position of the true zero point. The beam must swing freely during the observation: the zero is never to be read with the beam at rest.

This observed zero point may lie a little to the right or to the left of the marked zero. Note down its distance, in scale divisions, from the marked zero. If it lies to the right, prefix to the number of divisions the plus (+) sign; if to the left, the minus (−) sign. The zero of any one balance changes, and must be redetermined every time a weighing is made.

Place a 10 g. weight in each pan [Note 22, below], and determine the zero as before. Add the .01 g. weight to the right-hand pan, and find the reading about which the pointer now oscillates. The difference in reading between this point and the last determined zero point gives the deflection due to the .01 g. weight. It may be used for estimating weights less than .01 g.

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Note 22. — Great care must be taken in the **use of the balance and weights.** The pans of the former must be let down upon their supports when not in use and every time weights or other objects are to be added or removed. All objects to be placed upon the pans must previously be carefully cleaned and dried. Solids are placed upon a watch-glass or upon a piece of glazed paper, and never directly upon the pans. The weights must be lifted from their case by means of forceps, never by the fingers. They are usually placed on the right-hand pan, the objects to be weighed on the left.

Note 23. — In reckoning results, count first by the places vacant in the box, and check by counting the weights themselves. This will enable you to avoid the commonest error in weighing. Finally record the weights in the notebook, or laboratory outline, and never upon loose sheets of paper, as loss of the latter will necessitate a repetition of the entire experiment.

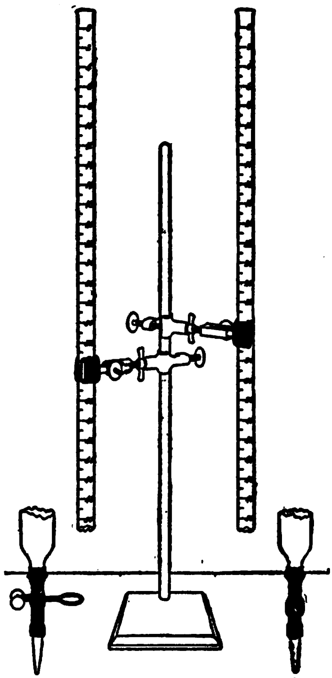

Fig. 2

7. Measuring Vessels [Quant.].

a. Fit a burette (Fig. 2) with a short piece of rubber tubing and glass nozzle (see **5**). The withdrawal of liquid from the burette is regulated by a pinch clamp upon this rubber connection, or by placing a small piece of glass rod (with fire-polished edges) in the middle of the rubber tubing to choke the bore. In this latter case, pinching the tubing surrounding the glass rod will permit the liquid to flow at any desired rate from the nozzle.

b. Support the burette upon a ring-stand by means of a clamp. Now fill the burette with distilled water, drawing off a portion to insure the complete removal of air from the rubber tubing and nozzle. The last bubble of air may be removed by turning the nozzle upward while the water is allowed

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to flow. Read the height of water by observing the lower side of the meniscus and estimate to tenths of a division.

Clean and dry a small beaker carefully and weigh it [Quant.]. Allow 10–20 c.c. of the distilled water to run from the burette into the beaker, read the new level of the water, and ascertain the volume taken by subtracting the readings. Weigh the beaker again and ascertain the weight of the water by subtraction. Calculate from your figures the weight of 1 c.c. of water. Keep the beaker and contents for use in *c*.

c. Place some distilled water in the graduated cylinder and read its volume. Pour about 10 c.c. of this water into the beaker (already partly filled with water), read the volume of the remainder, and find by subtraction the volume poured out. Now weigh the beaker once more and find the weight of this water by subtracting the previous weight. Calculate the weight of 1 c.c. of water.

Is measuring volume by burette or by cylinder more accurate (1 c.c. of water at 4° C. weighs 1 g.), and why?

d. Measure by means of the cylinder, roughly, the volumes of water your flasks and beakers hold, and record the figures. Fill the vessels to a convenient height for use, and not to the brim.

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CHAPTER II.

CHARACTERISTICS OF CHEMICAL PHENOMENA.

8. Qualitative Study of Chemical Phenomena.

a. Rub a pinch (about 0.5 g.) of powdered roll sulphur with a very small globule of mercury (use the dropper) in a mortar (?). When the mass has been intimately ground together for about five or ten minutes and no particles of mercury are longer observable, place it in a dry test-tube and add about 3 c.c. of carbon disulphide [CARE. Keep away from flames], a solvent for the free sulphur. Shake well (do not apply heat) and then pour off the clear solution into the sink [Hood. Note 25, below]. Repeat, shaking well and pouring away the clear liquid. Continue this operation until a sample of the decanted liquid fails to give any sulphur by spontaneous evaporation upon a watch-glass. What is the product remaining in the tube [R 657]? By means of a few c.c. of carbon disulphide wash this product out upon a filter paper [Note 24, below] and allow it to dry. To show the composition of this substance place it in a small dry test-tube and heat strongly over a flame. What odor is noticed at the mouth of the tube? What product is found to sublime upon the walls of the test-tube? Rub the sublimate with a glass rod (?). What characteristics of chemical change have you noticed in the above experiment?

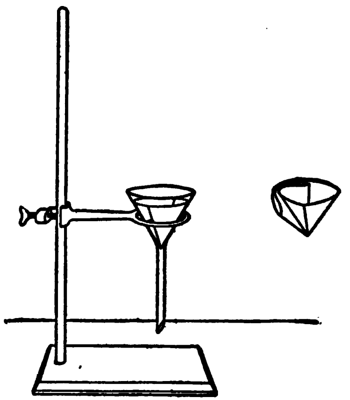

Fig. 3

Note 24. — Cut from a sheet of **filter paper** a piece 7 cm. (3 inches) square. Fold the square twice in directions at right angles to one another, so as to obtain a square of one-fourth the previous area. Cut off the loose corners with scissors so that a quadrant is formed. Open the folded paper so that a cone is produced (Fig. 3), and place the cone in a dry glass funnel. Smaller or larger pieces of paper are taken according to the amount of the precipitate or

of the liquid to be filtered, the smallest size that will serve the purpose being preferred. The funnel must be chosen so that the filter paper, after being trimmed and placed in position, does not quite reach the edge, much less project above it. While in use, the funnel is placed in a ring on the stand, and is not to be held in the hand.

Note 25. — Pour away all ill-smelling substances, like carbon disulphide, in the sink in the hood and not in the ordinary sinks or jars.

b. Gunpowder is made from saltpeter (potassium nitrate), roll sulphur, and charcoal. Bring specimens of these three substances on watch-glasses from the side-shelf, and examine them with respect to properties which can be used for recognition and separation [R 36, 37, 39], such as appearance and solubility in various solvents. Try the solubility of each in distilled water and in carbon disulphide, using in the latter case thoroughly dried test-tubes [Notes 25 and 26]. Do not judge of solubility by the eye, but filter the mixture [Note 24], catch a few drops of the liquid on a watch-glass, evaporate, and see whether there is any greater stain on the glass than the pure solvent would itself have left. The taste (?) of the saltpeter is a characteristic property.

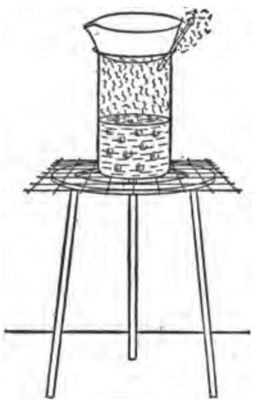

Fig. 4

Now place about 1 g. of gunpowder in a large test-tube and add 5–10 c.c. of water. Shake well (after closing the test-tube with the thumb), warm gently, and filter [Note 24]. Evaporate the filtrate upon a water bath or over a beaker of boiling water (Fig. 4). Describe and name the residue. Dry (why ?) the filter paper and its black contents over a radiator or in a drying oven. Shake the dried product with cold carbon disulphide in a dry [Note 26] test-tube, filter, and allow the filtrate to evaporate [Hood] spontaneously (?). What remains upon the paper? Did any chemical change occur during the manufacture of gunpowder?

Why are the ingredients of gunpowder pulverized so finely and mixed so intimately?

Note 26. — To **dry test-tubes** or flasks **quickly** after recent washing, warm them slightly in the Bunsen flame, connect with

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§ 9.

	Dish No. 1.	Dish No. 2.
Wt. of dish with lead (silver)		
Wt. of dish, empty		
Wt. of lead (silver)		
Wt. of dish with lead (silver) chloride		
Wt. of dish with lead (silver)		
Wt. of chlorine		
Wt. of lead (silver)		
Wt. of chlorine		
Wt. of lead (silver) chloride		

	No. 1.	No. 2.
Per cent lead (silver) (x)		
Per cent chlorine (x')		

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the air supply of a blast-lamp a piece of glass tubing long enough to reach to the bottom of the vessel, and allow a gentle stream of air to flow through the tube and vessel.

9. Law of Definite Proportions * [Quant.].

a. Obtain two pieces of pure lead of different sizes, about 0.5 g. and 0.6 g. respectively. Clean and dry two evaporating dishes, taking care to remove any paper labels which may be attached to them, and weigh each with care [Quant., balance]. Place one piece of the lead in each and weigh again. The difference will give the exact weight of the lead. Be careful in your notes, and in handling, to distinguish the dishes from one another.

Dilute 7 c.c. of concentrated nitric acid [Desk] with 14 c.c. of water in the graduated cylinder and add to the lead in each dish 10 c.c. of the diluted (1:2) nitric acid. Cover each dish with a watch-glass, convex side downward, and set upon the water bath. When the action is over, and the lead has entirely disappeared, rinse the lower surface of each watch-glass into the dish by means of a little water from the wash-bottle. Then add to the contents of each 5 c.c. of pure [Side-shelf] dilute hydrochloric acid. This causes the precipitation of a compound of lead and chlorine whose weight is next to be determined. To accomplish this, the water and other substances present (except the lead chloride) being all volatile, the mixture is dried by evaporation on a water bath. An extra Bunsen burner [Storeroom] and two beakers containing water may be used as baths, as in Fig. 4 [Hood]. A match inserted between the dish and the beaker permits escape of the steam and prevents the possible upsetting of the dish by the vapor. When the contents of the dishes are dry, moisten the contents of each with 2 c.c. of pure [Side-shelf], concentrated hydrochloric acid and dry once more. Now transfer the dishes, one at a time, to the clay triangle supported on the ring-stand, and heat the whole residue cautiously with a small Bunsen flame. Watch it narrowly and do not allow any of it to melt. When the dishes are cold, weigh each again with care. The increase in weight over the previous value in each case gives the weight of chlorine which has combined with the known weight of lead.

* Before beginning, always endeavor to ascertain the object of each experiment. By this means confused work and much waste of time will often be avoided, and significant facts to be observed and recorded will not escape notice. Consider, first, carefully the title, as it will usually indicate the object of the exercise. If the title is not at once fully understood, look up the topic in a reference book before going further.

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Calculate from each of the two sets of data the percentage of lead (x) and of chlorine (x') in lead chloride:

$$\text{Wt. of lead used} : \text{Wt. of lead chloride} :: x : 100.$$

$$\text{Wt. of chlorine found} : \text{Wt. of lead chloride} :: x' : 100.$$

Compare the results of the two measurements and interpret.

b. To secure almost ideal results, two pieces of pure silver foil of about 0.5 g. and 0.6 g. should be substituted for the lead in *a*.

Dilute 5 c.c. of concentrated nitric acid [Desk] with 5 c.c. of distilled water in the graduated cylinder and add to the silver in each dish 5 c.c. of the diluted (1:1) acid. When the action is over, and the cover-glasses have been rinsed, as in *a*, add 2 c.c. of pure [Side-shelf] dilute hydrochloric acid to the contents of each dish. This causes precipitation of a compound of silver and chlorine. Evaporate the liquids to dryness [Hood] and heat the residues at once until signs of melting are seen. Weigh each dish. The increase in weight over the previous value in each case gives the amount of chlorine which has combined with the known weight of silver.

Calculate from each of the two sets of data the percentages of silver (x) and of chlorine (x') in silver chloride:

$$\text{Wt. of silver used} : \text{Wt. of silver chloride} :: x : 100.$$

$$\text{Wt. of chlorine found} : \text{Wt. of silver chloride} :: x' : 100.$$

Compare the results of the two measurements and interpret.

Before cleaning the dishes, transfer the silver chloride to the bottle for silver waste.

c. Clean and dry two evaporating dishes, taking care to remove paper labels which may be pasted upon them. Weigh each dish [Quant., balance]. Place in each some sodium-hydrogen carbonate, in the one about 1 g. and in the other about 2 g., and weigh again. Treat both alike, as follows: Dissolve the solid in pure dilute hydrochloric acid [R 93], adding little by little and covering with a watch-glass between successive additions to avoid loss by spirting. When the solid has wholly dissolved, wash the watch-glass over the dish, and evaporate [Hood] the contents of the latter on the water bath, or on a beaker of boiling water (Fig. 4). (Avoid loss of time by borrowing a second Bunsen burner and gas tubing temporarily from the storeroom.) Allow the dishes to cool, and weigh. To make sure that the drying was complete, heat once more for

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half an hour and weigh again. This precaution is taken in all experiments of this kind. The product is common salt. Calculate the proportion of carbonate taken to salt produced thus:

$$\text{Wt. of carbonate} : \text{Wt. of salt} :: 1 : x.$$

Compare the two values of x found from the two differing quantities of the carbonate and interpret.

What physical property of hydrochloric acid permits use of an excess of the acid without damage to the result? What form of statement of the law is verified directly by this experiment?

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CHAPTER III.

OXYGEN.

10. Sources (p. 11, footnote). Heat small quantities of barium peroxide, lead dioxide, potassium nitrate, silicon dioxide (sand), and manganese dioxide (dry this before use by heating it for a few minutes in a porcelain crucible) separately in a hard glass test-tube [Note 27]. Observe whether any gas is given off, and apply the test of the glowing splinter of wood [Note 28]. If the Bunsen flame proves inadequate, try the blast-lamp. Note any changes in appearance during the heating and describe the residues [Note 29]. Clean the test-tube carefully with hot nitric acid [CARE] and dry it [Note 26, p. 10] after each experiment.

Note 27. — Use the clamp and ring-stand to support the tube, or grasp it by means of a strip of folded filter paper (Fig. 5). In either case it must be kept in a horizontal position, otherwise condensed moisture may run down and cause it to crack.

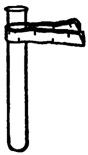

Fig. 5

Note 28. — Use a long splinter of pine wood [Side-shelf] bearing a spark at one end (why not an ordinary match?). Such a splinter is at once kindled by oxygen.

Note 29. — Beginning with this chapter include in your notes **equations** for all the chemical changes you observe. When no change is observed, do not attempt to give an equation until otherwise instructed (Chap. IX). In the present experiments the formulæ of the materials used will have to be sought in the text-book. The formulæ of the products will also be sought in the book after the physical properties of the product and the evolution or non-evolution of oxygen have been noted and an indication of what to seek for has thus been obtained. For other information in regard to the note-book, see the "General Instructions," Notes 1–5, p. 1.

11. Catalytic Action.

a. Place in a test-tube a little potassium chlorate, fix the tube in a vertical position by means of a burette clamp attached to the ring-stand, and melt the substance at the lowest temperature at which this is possible (patience!). Note whether there is evidence of the evolution of oxygen. Now throw into the molten material a pinch of powdered manganese dioxide (?) [Note 2, p. 1], keeping the face out of the path of anything

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which may accidentally be projected from the tube. Interpret [R 65, 75].

b. Devise a way of showing that the manganese dioxide, used as in *a*, remains unchanged after the action, and that it is the potassium chlorate that loses its oxygen, and try it (?). Consult the instructor in regard to the details of your plan before executing it.

12. Preparation. Mix on paper about 5 g. of potassium chlorate and 3 g. of powdered, dried (see **10**) manganese dioxide. Place the mixture in a hard glass test-tube provided with a one-

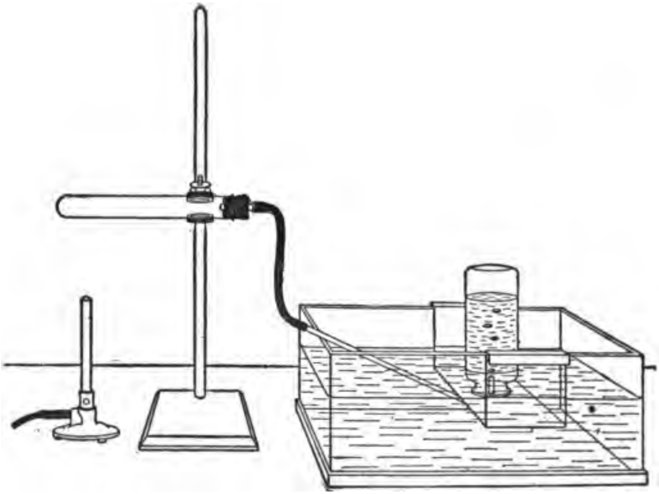

Fig. 6

hole cork and delivery tube (Fig. 6). Test the apparatus to see that it is air-tight. (In this instance, place the end of the delivery tube in the mouth, withdraw some of the air by suction, and note whether or not the tongue will adhere to the end of the tube. If it will not, there is a leakage which must be remedied.)

Clamp the test-tube on the ring-stand and heat carefully, so as not to cause too violent an evolution of oxygen. Collect four bottles of the gas over water in a pneumatic trough, taking care to remove the delivery tube from the water as soon as the bottles are full of oxygen (why?). The test-tube may be cleaned by allowing it to soak in water.

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13. Properties [Note 5, p. 1].

a. Place a very small amount of sulphur in a deflagrating spoon, ignite it and then lower into a bottle of oxygen (?) [Note 2, p. 1].

Remove the spoon, add a little water to the jar, close the mouth with the hand and shake (?). Test the water with blue litmus paper or solution [R 70–71, 355].

b. Place a little red phosphorus in the spoon, ignite it, and lower into the second bottle (?).

Proceed as in *a.* Test with blue litmus [R 70–71].

(If yellow phosphorus is used, it must always be cut under water and handled with forceps. Great care must be taken not to touch it with the hand, as it catches fire easily, and causes very severe burns. Red phosphorus is safer, and should be employed if available.)

c. Lower a splinter of glowing charcoal into the third bottle, holding it in the tongs or wrapping the end of a piece of copper wire round it (?).

Proceed as in *a* (use no litmus), and cover the mouth of the bottle with a glass plate. Add some lime-water (calcium hydroxide) and shake again [R 481–482] (?).

14. Slow Oxidation of Metals. Devise a way of showing that air loses a part of its substance (not, e.g., that the iron gets heavier, but that the air diminishes in amount) when moist iron powder rusts, and try it. Submit your arrangement to the instructor for criticism before using it.

15. Weight of a Liter of Oxygen [Quant.] (p. 11, footnote).

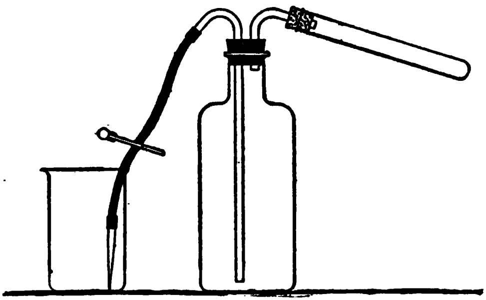

Fig. 7

a. Powder some potassium chlorate, and dry it on a watch-glass on the radiator, or high above a small Bunsen flame, or in a drying oven. Construct an aspirator (Fig. 7), using the

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§ 15 a

Wt. of tube with chlorate	
Wt. of tube with residue	________
Wt. of oxygen	________
Wt. of beaker with water	
Wt. of beaker	________
Wt. of water	________
Temp. in lab.	________
Temp. near barometer	
Barometric reading	
Correction	________
Barometer (corr.)	
Aqueous tension at temp. of lab.	________
Partial press. ox.	________

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1-liter bottle, and connect it with a hard glass test-tube. Fit a nozzle to the rubber tube and slip a pinch clamp over the outlet tube (syphon) in readiness for closing, at a later stage, the rubber tube that connects the two glass tubes. Having inserted the stopper tightly and connected the test-tube, test the apparatus to see that all the joints are air-tight [Instructions: Place some water in the bottle, blow a few bubbles of air into the apparatus through the syphon, and observe whether the water remains permanently elevated in the vertical tube. Absolute certainty that the apparatus is air-tight must be reached before proceeding further].

Carefully weigh the hard glass test-tube, then place in it between 1 g. and 2 g. of potassium chlorate and weigh again. More than 2 g. is not needed, less than 1 g. will not be sufficient. Subtraction gives the exact weight that has been employed. Fill the bottle almost, but not quite, to the shoulder with tap water. After reattaching the test-tube make sure that the apparatus is once more air-tight, by repeating the above-described test. Next fill the syphon and nozzle completely with water by blowing sharply through the latter, and close the clamp. Allow the nozzle to touch the bottom of a beaker (400 c.c.) containing some water. Now open the clamp and raise the beaker till the levels of the water in this and the bottle are the same, and the gaseous pressure therefore alike in both. Close the clamp again, empty the beaker and replace it in position.

Open the clamp once more and decompose the compound slowly by heating, catching in the beaker the water driven over by the gas. During the earlier stages a smoke, consisting of solid particles, will arise. This must on no account be driven into the connecting tube, as all the solid must remain in the test-tube to be weighed (why?). Suspend the heating as often as may be necessary to let this smoke settle. During such intervals of waiting see that the nozzle is constantly immersed in the water that has already passed over (why?). Stop heating if the tube shows signs of softening [Note 30, below] or when the decomposition is complete. For the purpose of this experiment (see **15** *b*) it is not necessary that the action should be carried to completion. If, when the heating is stopped, the nozzle is not under water, raise the beaker until it is well covered. Allow the whole apparatus to stand until it has reached the temperature of the air. Some water will return to the bottle by the syphon during the cooling. Admission of air to the syphon through the nozzle at any stage will prevent this transference, which is essential to the success of the ex-

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periment. Equalize the levels of the water in both vessels by raising or lowering the beaker, and then close the clamp.

Measure the volume of water in the beaker by weighing the vessel, first with and then without the water, upon the laboratory scales. The difference in weight in grams represents with sufficient accuracy the number of c.c. of water displaced and hence of oxygen evolved in the operation (what of the air originally in the apparatus?). Weigh the test-tube once more with care [Balance]. Observe at the same time the temperature in the laboratory to learn the temperature of the oxygen, and read the barometer [Note 31, below] to learn the pressure of the air and therefore of the oxygen.

Subtract the aqueous tension (Appendix II) at the observed laboratory temperature from the barometric reading (corr.) to get the true (partial) pressure of oxygen in the bottle. Reduce the volume by rule to 0° and 760 mm. The weight of this volume of oxygen is obtained by subtracting the weight of the residue in the test-tube from the weight of the potassium chlorate originally taken. Calculate by proportion from the data obtained the weight of 1 liter of oxygen (x):

$$\text{Vol. of ox. found} : \text{Wt. of ox. found} :: 1000 \text{ c.c.} : x.$$

Calculate also the volume occupied by 32 g. of oxygen. To what class of gases would the use of the aspirator be confined for purposes like the above?

Note 30. — To avoid softening of the glass, through overheating, watch the color of the Bunsen flame. The blue flame is tinged with a yellow color (caused by compounds of sodium in the glass) where the flame encounters the overheated part of the tube.

Note 31. — When the barometer is read, the height must be "corrected" to that of a column of mercury at 0° (Appendix I).

b. Detach the hard glass test-tube from **15** *a* and drive off the last traces of oxygen by heating strongly every portion of the tube to which any of the residue adheres. Allow it to cool and weigh. Obtain the weight both of the residue (potassium chloride) and of the total oxygen, by difference.

Assuming the formula of the chloride to be KCl, that of the chlorate is $KClO_x$. The formula weight of KCl being 39.15 + 35.45 = 74.6, find the formula weight of O_x by the proportion:

$$\text{Wt. of KCl found} : \text{Wt. of oxygen found} :: 74.6 : y,$$

where $y = O_x$. This will be a multiple of 16 by a whole number (why?) if the measurement has been carried out successfully. What formula do you find for potassium chlorate? Write the equation for the decomposition of the chlorate.

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§ 15 *b*

Wt. of tube with chlorate	
Wt. of tube empty	
Wt. of chlorate	
Wt. of tube with chloride	
Wt. of tube empty.	
Wt. of chloride	

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CHAPTER IV.

HYDROGEN.

16. Interaction of Metals and Acids.

a. Place a few small pieces of each of the metals, tin (granulated), copper (a nail), iron (filings), zinc (gran.), lead (gran.), aluminium (turnings), and magnesium (wire) in separate test-tubes. Place in the measuring cylinder 20 c.c. of pure [Side-shelf], concentrated hydrochloric acid [R 93] and add an equal volume of water. Add 5 c.c. of the mixture to the contents of each test-tube (?). Observe each case critically [Note 32, below] and record the results [Note 29, p. 14], noting the order of the metals in respect to activity. Notice the effect of heating, if no action occurs in the cold. If heating seems to produce gas, remember that it may be hydrogen chloride (why?) or steam and not hydrogen. The presence of hydrogen may be inferred from continued effervescence when heat is not being furnished, and may be proved by the slight explosion which follows when a light is brought to the mouth of the tube. But hydrogen will not burn when mixed with much air or with other vaporous substances (why ?). After the action has ceased, filter any one of the solutions and evaporate [Hood] it to dryness on the sand bath (?).

Can you give any grounds for the belief that the hydrogen comes from the acid and not from the metal or the water?

Which metals, not used above, will displace hydrogen from dilute acids [R 362, and Appendix VII] ? In what ways, if at all, does the order of activity you have observed differ from that accepted by chemists?

In making the equations for these actions all that is needed, beyond the information given above and acquired by observation, is to find the formulæ of the products. These are not here to be sought by measurement, but in the text-book [R].

b. Ascertain the influence of the physical state of the metal on its apparent activity by adding some zinc dust to the same acid [R 111].

c. Place one small piece of *pure* zinc into each of two test-tubes and add diluted sulphuric acid [Desk] to both tubes. If little or no action takes place in the cold, try upon one tube the effect of heating (?). Try the effect of putting a platinum wire in contact with the zinc in the second tube (?). Notice

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where the hydrogen appears to come from, and explain [R 96]. Withdraw the platinum wire, add a drop of cupric sulphate solution, and shake (?). Is the solution still blue, and is the zinc still silvery? What is the substance upon the zinc [R 361], and what effect does it produce upon the apparent activity of this metal? Explain.

d. Now compare (?) the behavior of concentrated sulphuric acid [Desk] with that of the diluted acid used in **16** *c*, by placing some zinc (gran.) in a test-tube and adding enough of the concentrated acid to cover the metal (why not more?). After noticing the effect in the cold (?), apply heat (?). What products are formed [Note 32]?

e. Try the interaction of acetic acid with zinc (gran.) or iron (filings). Apply heat, if necessary.

Note 32. — In observing an interaction a chemist first mixes the substances thoroughly by shaking. If nothing occurs, he then heats. If his eye detects evidence of the production of a gas or vapor, he finally smells the contents of the tube. Apply these three methods of observation to *d* before drawing any conclusion.

17. Other Methods of Obtaining Hydrogen.

a. Describe the result of throwing pieces of sodium and of potassium into water, as you recall having seen it [Classroom]. What other metals displace hydrogen from water [R 362]?

b. Fit a test-tube with a one-hole cork and delivery tube (Fig. 6). Pulverize about 2 g. of sodium hydroxide, mix it intimately in the mortar with about 3 g. of zinc dust, and place the mixture in the test-tube. Insert the cork and delivery tube, test the apparatus for air-tightness (**12**), and clamp the tube in a horizontal position (why?). Heat the mixture and collect the gas (?) over water (Fig. 6) in a test-tube. If the tube should crack [CAUTION!] cease heating at once. To learn whether the gas is combustible, carry the test-tube, when full of the gas, mouth downward to a flame (?).

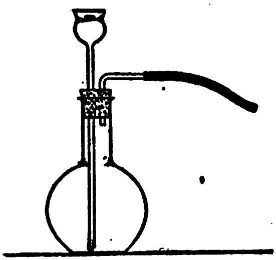

Fig. 8

18. Preparation of Hydrogen [Same apparatus is used for **19** and **20**]. Fit a 250 c.c. flask with a safety tube and exit tube (Fig. 8), and test for air-tightness. Place in the flask some commercial, granulated zinc, close the apparatus, and attach to the L-shaped exit tube, by means of a short piece of rubber

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tubing, a longer glass delivery tube. Now pour 30–40 c.c. of dilute hydrochloric acid [Desk] through the safety tube. Test the issuing gas until it is found free from air [Instructions: The gas must not be ignited at once or the apparatus will be blown up (whence comes the air mixed with the hydrogen?). Collect samples of the gas from time to time by raising the delivery tube and inserting it to the upper part (why?) of a test-tube held in an inverted position, and then bringing the mouth of the tube (still inverted) to a distant flame. When the gas contained in the test-tube, after the first explosion of the part nearest to the mouth, burns quietly, the gas is free from air. Call an instructor to inspect the test]. Keep the apparatus in operation for use in **19** and **20.**

19. Properties of Hydrogen.

a. By collection over water in the pneumatic trough, fill a test-tube with hydrogen. Using this, and a similar test-tube filled with air, show by an experiment that hydrogen is lighter than air (?).

Fill another test-tube with hydrogen and apply it closely, mouth downward, to a test-tube of air, mouth upward. Allow the tubes to remain in this position for three minutes, then bring first the lower and then the upper tube quickly to a flame (?). What fact about diffusion does the result illustrate?

b. Fill another test-tube with hydrogen, as in *a*, and, holding it mouth downward, insert into the tube a burning match. Does the match continue to burn? Explain.

c. Remove the glass delivery tube, and connect a glass nozzle with the exit tube of the generating flask. Press the mouth of the nozzle close against the side of a cold, dry beaker. If moisture is deposited (what is its source?), fill a U-tube with calcium chloride [R 100] and connect it between the exit tube and the nozzle. Does the gas now deposit moisture upon a beaker? If not, ascertain that the issuing gas is not explosive (see test in **18**), and set fire to it. What is the color of the flame? Does the color change, and, if so, why? Hold a cold, dry, inverted beaker over the flame. What is deposited on the beaker? Why did we use dried hydrogen for this experiment? Keep the apparatus in operation for **20**, unless a Kipp's apparatus is available or hydrogen is furnished in the laboratory.

Remove the nozzle with its rubber connection and push the latter tightly into the end of the gas tubing furnished with the Bunsen burner. Connect the other end of the tubing with the illuminating-gas supply. Turn on a gentle stream of gas and set fire to it. Hold a cold, dry beaker over this flame (?). What inference in regard to illuminating-gas do you draw?

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20. Reduction by Means of Hydrogen [Two students working together]. Fit a hard glass tube, 25–30 cm. long and open at both ends, with perforated corks and short glass tubes (Fig. 9). Support it on the ring-stand by means of a clamp grasping it close to one end. Dry 1–2 g. of ferric oxide by heating in a porcelain crucible. Put the oxide into the porcelain boat and place the latter in the hard glass tube near the end remote from the clamp (why?), but not so near that the subsequent heating will char the cork. Insert the corks with their tubes. Connect the tube nearest to the boat with a Kipp's apparatus and drying bottle (Fig. 18) delivering dry hydrogen, or with the laboratory supply of the gas, or with the apparatus furnishing dry hydrogen used in **18**.

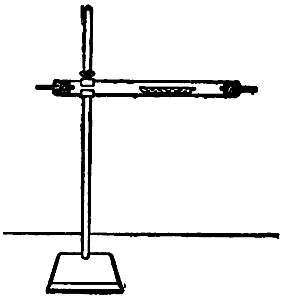

Fig. 9

Test the issuing gas to see that it is not explosive (see **18**) and repeat the test every time the apparatus is opened. Now heat the boat and contents, at first gently by waving the flame under the tube, and later strongly until the material is red-hot (what temperature is used [R 73] ?). Observe the effect upon the ferric oxide [R 756] (?). Does anything condense in the cooler end of the tube?

What is the action of steam upon heated iron [R 98] ? How do you reconcile this fact with that observed above?

Repeat the above experiment, using freshly heated aluminium oxide in place of ferric oxide, and otherwise following the directions exactly (?). If no effect is noticed after an oxide has been at a red heat for three minutes, absence of action may be inferred. How do you account for the result obtained with aluminium oxide? Which oxides are reducible by hydrogen [R 362] ?

What are the commercial and mineralogical names given to the two oxides used in these experiments [R] ?

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CHAPTER V.

WATER AND SOLUTION.

21. Purity of Water. Place a few drops of distilled water on a clean watch-glass (not an evaporating-dish. Why?) and evaporate on the water bath. Do the same with ordinary water. Observe whether any stains remain on the glasses (?). What class of impurities would leave no trace of their presence in this test?

22. Union with Oxides. Place a pinch of cupric oxide in a test-tube and wash it by shaking with a little distilled water and pouring off the liquid. Add more water and shake again. Test this latter solution with litmus paper (?). At the same time test a sample of the water with litmus paper and compare the tints. Repeat with barium oxide (?).

Recall the behavior of acid-forming oxides examined in **13**. Some oxides do not interact readily with water (which?). These oxides which do interact may be divided, according to the natures of the products they give, into two classes. What are those classes, and which oxides belong to each? What are the two classes of elements whose oxides belong to the two groups, respectively [R 119]?

23. Hydrates.

a. Heat some blue vitriol (p. 4, footnote) gently in a porcelain crucible (?). Allow a very small portion of the white powder to stand exposed to the air on a watch-glass (?). Dissolve the remainder by boiling with the minimum amount of water required to dissolve it, and set the solution aside (?). What chemical actions have taken place in these three operations?

b. [Quant.] Place small quantities (about 1 g.) of Glauber's salt and of blue vitriol in two porcelain dishes and ascertain the gross weight in each case. Allow the dishes and contents to remain for 24 hours or more and weigh again (?). Interpret the results [R 121].

c. Gently warm small quantities of barium chloride, potassium nitrate, magnesium sulphate, and potassium dichromate separately in dry test-tubes and notice whether they undergo any change [R].

Are all crystalline substances hydrates? Classify the substances you have examined into two groups with reference to this property.

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d. Take in a test-tube about 5 c.c. of commercial, concentrated sulphuric acid, place in it a crystal of blue vitriol and let the materials stand for an hour, or more (?) [R 388]. Now heat the contents of the tube to the boiling-point of the acid, holding the test-tube in a test-tube holder, keeping it far from the clothing, and taking care that none of the contents spirt out upon the hands or face [CAUTION: Sulphuric acid burns are very painful. Note 16, p. 2]. After the contents of the tube have settled, pour off the clear liquid into another tube. On the following day, examine the little, shining particles on the sides of the tube. What is their color, and condition? Of what are they composed [R 625]?

Are the compounds (such as cupric sulphate) which, in presence of water, yield crystalline hydrates, amorphous or crystalline in its absence? What is the true significance of the crystalline condition [R 123]?

e. Take a clean match-stick and, after dipping it in a solution of cobalt chloride, write upon a piece of white paper. After the writing is dry, warm the paper gently by waving it above a Bunsen flame (?). Now, breathe repeatedly upon the writing (?). Write equations for the actions that have occurred [R 759].

f. [Quant.] Put about 1 g. of crystals of gypsum in a weighed porcelain crucible and weigh again. Place the crucible on the clay triangle, heat to redness until no further loss in weight occurs, and determine by difference the loss in weight (water) and the weight of the calcium sulphate remaining.

The formula of gypsum must be $CaSO_4,xH_2O$. Assuming the formula-weights of calcium sulphate ($CaSO_4 = 136$) and of water ($H_2O = 18$) calculate from your data the value of x.

$$\text{Wt. of calcium sulphate} : \text{Wt. of water} :: 136 : x \times 18.$$

What is the formula of gypsum?

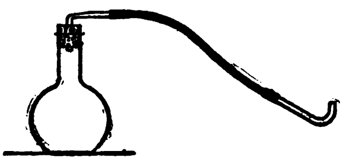

Fig. 10

24. Solution: Gases in Liquids. Half fill a 1-liter bottle with distilled water, cork, and shake vigorously till the water is saturated with air. Take the temperature of the water and also the barometric reading. Fit a small flask (100 c.c.) with a one-hole cork and delivery tube (Fig. 10) and measure its content up to the lower surface of the cork. Completely fill the whole apparatus, including the delivery tube, with the

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prepared water, and boil, collecting the gas in a small test-tube inverted over water. When no more gas comes over, equalize the levels of the water in the tube and trough (or beaker) and mark the level in the tube with a thin rubber ring (cut this from a piece of rubber tubing). Measure the volume which the air occupied. Correct the volume for the aqueous vapor present only, obtaining thus the volume of the air when dry and at the observed temperature and pressure. Calculate the volume of air dissolved by 100 c.c. of water at the observed temperature and pressure (?). What proportion of its own volume of air has the water dissolved?

25. Solution: Liquids in Liquids.

a. Take 5 c.c. of carbon disulphide in a dry test-tube [Note 26, p. 10], and add to it 5 c.c. of water, a drop at a time, shaking vigorously after each addition and observing whether at each stage the mixture is homogeneous or not (?).

b. Repeat, using 5 c.c. of ether with water (?).

c. Mark off on a narrow test-tube by means of the triangular file the points at which 10 c.c. and 20 c.c. of water stand, respectively. Empty the test-tube and pour in 10 c.c. of water, and then take 10 c.c. of alcohol in the graduated cylinder and add it to the water, a drop or two at a time, shaking vigorously after each addition and observing as before. Finally, compare the volume of the mixture with that of the components separately (?).

26. Solution: Solids in Liquids.

a. Select two large crystals of some soluble, colored compound, such as blue vitriol (or potassium dichromate). Choose crystals of approximately equal size and so large as to be just capable of being slipped into a test-tube. Reduce one of the crystals to a fine, uniform powder in the mortar. Note and account for the change in tint (?). Now place the crystal and the powder in separate test-tubes, and provide two corks which fit the mouths of the tubes. Add 20 c.c. of water simultaneously to each tube, and insert the corks. Read the time on a watch and shake the tubes simultaneously with vigor, noting the time at which the solid finally disappears in each tube (?). Account for the difference.

b. Reduce to a fine powder 10–15 g. of potassium dichromate, using the larger amount in warm weather, the smaller in cool. Prepare a saturated solution of the substance by placing it in a flask with 50 c.c. of water and shaking at intervals for ten minutes. So much of the solid must be taken that an undissolved residue remains.

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Take the final temperature of the solution. Now pour the clear solution into a burette attached to the ring-stand, filling the apparatus completely to the point of the nozzle with the liquid (7 *b*). Read the level of the lower side of the meniscus. Weigh [Quant.] a clean, dry evaporating-dish, run into it about 22–24 c.c. of the solution, and weigh [Quant.] the dish and contents. Read also the level of the meniscus and note the volume of solution used. Now evaporate the weighed portion of the solution completely to dryness upon a water bath, or on a beaker of boiling water, and weigh again. Determine by difference the weights of the dry dichromate here found, and of the water in which it was dissolved. Calculate from the data the weight of dichromate which would be dissolved by 100 c.c. of water at the observed temperature.

From the volume of the part of the solution evaporated, and the weight of dichromate found in it, calculate also the molar solubility [R 149] of potassium dichromate at the observed temperature. Compare the results with those which would be obtained with potassium chromate K_2CrO_4 (Appendix IV) (?).

c. Take about 6 g. of the dichromate and boil with 10 c.c. of water in a test-tube. Is the solubility at this temperature different? Allow the clear solution to cool (?). Explain the result. What sort of curve of solubility would this substance exhibit (Appendix V)?

Take about 6 g. of sodium chloride and boil with 10 c.c. of water in a test-tube. Pour the clear liquid immediately into another test-tube. Examine this when cool (?). Is salt much less soluble in cold than in boiling water? How would its curve of solubility differ from that of potassium dichromate?

d. Shake some powdered calcium sulphate with cold, recently boiled, distilled water. Ascertain whether any of the salt has gone into solution (**21**). Repeat with chalk (calcium carbonate), rejecting the water with which it is first shaken (?). Which of these substances do you find to be more soluble? What are the amounts of these salts dissolved by 100 c.c. of water at 18° [R Appendix IV]? In what ratio is calcium sulphate more soluble than calcium carbonate [R Appendix IV]? In what ratio is calcium chloride more soluble than calcium sulphate [R]? Which of all these substances are spoken of as "insoluble"?

e. Take about 10 c.c. of water in a test-tube, add to it not more than 1 c.c. of lead nitrate solution, and mix. Now add about 2 c.c. of dilute hydrochloric acid (?). Repeat, heating the mixture to the boiling-point before adding the hydrochloric acid (?). Examine this tube again, after the contents have

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cooled (?). Interpret the result. Is lead chloride an "insoluble" substance [R Appendix IV]?

f. Take about 10 c.c. of water in each of two test-tubes. To one portion add Glauber's salt, previously pulverized in a mortar, until, after shaking, a considerable excess remains undissolved. Saturate the other portion with anhydrous sodium sulphate in the same manner. Perform the last operation rapidly, taking care not to introduce any particles of the hydrate, and do not let the solution stand before use. Now decant the two liquids into clean test-tubes, disregarding the cloudiness of one of them. Then add a little of the anhydrous substance to the solution first made and a small crystal of Glauber's salt to the contents of the second test-tube and shake both (?). After a short time, examine the contents of each again (?). Interpret the results [R 160–161].

g. Two immiscible solvents. Place one small particle of iodine in each of three test-tubes and add to one water, to the second potassium iodide solution, to the third carbon disulphide, and shake each (?). If any iodine remains undissolved, pour off that solution into a clean test-tube. Now add a drop or two of carbon disulphide to the first two solutions, shake again (?), and describe carefully what seems to have happened. Deduce from this the relative solubility of iodine in the three solvents.

27. Properties of Solutions: Vapor pressure and Boiling-Point.

a. Place some dry potassium carbonate (or pulverized calcium chloride) in a small beaker or crucible. Set the vessel in an evaporating dish containing water, and invert over it a larger beaker so that the edge of the latter is under the liquid. Examine the material from day to day (?). Remembering that there is moisture upon the surface of even "dry" bodies, and that therefore a solution of potassium carbonate was present with the solid, explain the change [R 162]. To what class of substances do those which deliquesce all belong? Is deliquescence a physical or a chemical phenomenon?

b. Fix a test-tube containing about 10 c.c. of water in a clamp upon the ring-stand. Suspend the thermometer from a ring by means of a thread, in such a way that the bulb is immersed in the water. Boil the water, using a small Bunsen flame, and read the temperature (?). Now add to the boiling water about 2–3 g. of dry calcium chloride, and, after solution is complete, read the temperature of boiling again (?). Add another, equal portion of calcium chloride and repeat the temperature reading after the whole has dissolved (?). Explain [R 162].

c. If pulverized ice were to be added to water until the

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solid no longer melted, what would be the temperature of the mixture? If ice were to be added to the aqueous solution of some substance, until the ice no longer melted, how would the temperature differ from that of water and ice? Why does this difference exist [R 163]? Why does salt thrown upon ice cause the latter to melt [R 164]?

28. Properties of Solutions: Volume Changes and Thermal Effects.

a. Recall the change in volume observed in **25** *c* when alcohol and water were mixed (?).

b. [Quant.]. Take about 25 g. of potassium carbonate and determine its weight to the nearest tenth of a gram. Assuming the specific gravity of this substance to be 2, calculate the volume of the amount you have taken (?). Place in the graduated cylinder exactly 85 c.c. of water and take its temperature. What is the sum of the volumes of the water and the carbonate, separately? Add the weighed specimen of potassium carbonate to the water, dissolve by repeated inversion of the cylinder, closing the mouth of the latter with the hand, and read the volume of the solution (?). Read also the temperature of the solution immediately. Is there a change in volume, or in temperature, on dissolving two substances in one another?

What relation exists between the sign of the thermal effect when a substance is dissolved in a nearly saturated solution of the same substance, and the change of solubility with temperature [R 260]? What do you infer in this case?

c. Examine the solubility curve of anhydrous sodium sulphate [R 158] (?). Will this compound give out or absorb heat in dissolving in water [R 260]? Verify your conclusion by trying the experiment (?).

d. Repeat *b*, using about 25 g. of ammonium chloride (sp. gr. 1.5). Make the same observations and answer the same questions.

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CHAPTER VI.

CHLORINE AND HYDROGEN CHLORIDE.

29. Preparation of Chlorine [Hood].

Experiments **29** *b* and **30** must be accomplished at one exercise. **29** *a* may be postponed to facilitate this.

a. Prepare some strips of filter paper by dipping them in starch emulsion [Side-shelf] to which you have added one drop of potassium iodide solution.

Place small quantities of finely powdered manganese dioxide, potassium chlorate, lead dioxide, and pure litharge in as many test-tubes, and add a little commercial, concentrated hydrochloric acid [Desk] to each. Notice the color (?) and odor (?) of the gas in each case. If no action takes place in the cold, apply heat. Dip into the gas in one of the test-tubes a strip of the prepared paper (?). How do you account for the difference in the behavior of the two oxides of lead? Do all compounds containing oxygen give free chlorine in this way? If not, state what is common to those which do.

b. Fit up a 250 c.c. generating flask, as in Fig. 11 with a dropping-funnel (or substitute **36** *b*) and an L-shaped glass tube attached to the exit tube. Use the shortest possible rubber connections here and in **31** (hydrogen chloride), as rubber tubing is destroyed by these gases. Test the apparatus to see that it is air-tight. Place in the flask about 20 g. of dry potassium permanganate, and fill the globe of the dropping-funnel with diluted, commercial, concentrated hydrochloric acid (1 Aq. : 3 acid). Allow the delivery tube to dip to the bottom of a small beaker containing a little sodium hydroxide solution [Desk]. Now admit the acid drop by drop, regulating the flow so that too rapid a stream of gas is not produced. The complete displacement of the air in the flask will be recognized by the color of the contents and the fact that the bubbles of pure chlorine are completely absorbed by the sodium hydroxide.

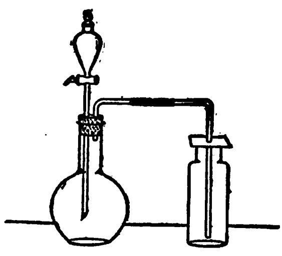

Fig. 11

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When the air has all been displaced, fill three dry bottles and one dry test-tube with the gas by downward displacement, observing the following precautions: Provide a piece of stiff paper or card, perforated with a hole for the reception of the delivery tube, to cover the bottles during the filling, and cover the vessels with glass plates as soon as they are full. See that the delivery tube reaches to the bottom (why?) of each vessel during the filling. Replace the end of the delivery tube in the sodium hydroxide when all the vessels have been filled. When the experiment is over, pour the contents of the generating flask into the sink in the hood, and not into one of the sinks in the open laboratory, and wash down with much water.

30. Properties of Chlorine [Hood].

a. In one bottle of the gas scatter a pinch of finely powdered antimony [R 715] (?).

b. Take a clean piece of sodium [From Instructor] and cut from it a very thin slice not more than one-half inch square (fingers and knife used in handling sodium must be dry!). Introduce this piece into a bottle of chlorine (?) and cover at once with a glass plate. Examine after half an hour. If any of the metal remains unattacked, scrape off the white deposit and place it upon a watch-glass, and throw the sodium into the sink in the hood. Add the material on the watch-glass to that in the bottle and dissolve in 2 c.c. of water. Allow the solution to stand in a watch-glass until it dries, and examine the crystals with a lens (?).

c. Connect a glass nozzle with the illuminating-gas supply, and lower a small, burning gas-jet into the third bottle (?). Blow the breath into the bottle after withdrawing the jet (?).

d. Fill a test-tube with hydrogen from a Kipp's apparatus or from the laboratory supply. Bring this tube mouth to mouth with a tube of chlorine and mix the gases by repeated inversion. (Take care not to expose the mixture to direct sunlight.) Hold the mouth of each tube to the Bunsen flame (?). Close the mouth of one tube quickly with the thumb, add a few drops of water, shake, and test the solution with litmus paper (?).

31. Preparation of Hydrogen Chloride.

a. [Hood] Place small quantities of ammonium chloride, barium chloride, mercuric chloride, and sodium chloride in as many test-tubes, and add a few drops of concentrated sulphuric acid [Desk] to each (?). Describe what happens in each case. Blow moist air across the mouth of the test-tube (?). Lower a glass rod dipped in ammonium hydroxide solution into each [Note 33, below]. Try the effect of heating. Remember that

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the solubility (physical) of the substance in sulphuric acid will largely determine the speed of the action. In case of difficulty, therefore, take a fresh sample of the solid, pulverize it finely, and shake with the acid for some minutes before heating and testing. Arrange the substances in the order of apparent activity.

b. To a pinch of finely powdered sodium chloride add a strong solution of phosphoric acid and heat if necessary [R 179] (?). Test with ammonia as before. The above remark about solubility applies also to this case.

Why is hydrogen chloride displaced completely in *a* and *b* by these acids under these conditions [R 180]?

c. [Hood] In a 250 c.c. flask (Fig. 11), fitted with dropping-funnel (or substitute, **36** *b*) and L-shaped delivery tube, place about 30 g. of common salt. Admit concentrated sulphuric acid through the funnel. Collect the gas in three dry bottles by downward displacement (using a perforated square of paper or card as in the case of chlorine), cover, when filled, with glass plates and reserve for **32.** Place about 10 c.c. of distilled water in a test-tube, attach a nozzle to the delivery tube, and allow the gas to bubble into this for a few minutes (?). Reserve the aqueous solution also for **32.** Write equations for the two possible interactions of salt and sulphuric acid. Which of the two takes place under the above conditions?

Note 33. — The use of ammonia is not a specific test for hydrogen chloride. It can be used only for ascertaining the presence or absence of any one of several gases, usually of acidic character, which are capable of uniting with ammonia.

In writing the equation here, and whenever the same test is used, consider whether the interaction took place with the liquid on the rod (containing NH_4OH), or with the gas (NH_3) given off by this liquid. Note the odor of this gas (?).

32. Properties of Hydrogen Chloride and of Hydrochloric Acid.

a. Invert one of the bottles of the gas in a dish of water (?). Relate this property to that observed on blowing moist air into the gas (**31** *a*). If any gas remains, what should you expect it to be? Test your conclusion experimentally.

b. Pour a little ammonium hydroxide solution on a strip of filter paper and plunge this into the second bottle (?) [Note 33, above]. Describe the difference between these fumes and those formed by the action of moist air upon the gas (**31** *a*).

c. Devise a way of proving, in a rough way, that the gas is heavier than air, and use the third bottle of gas for carrying it out.

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Perform the following experiments with the aqueous solution prepared in **31** *c*.

d. Test the solution with litmus paper.

e. To a part add a granule of zinc (?).

f. To a part add a crystal of sodium carbonate [R 480] (?).

g. Dilute the remaining portion of the acid solution with an equal volume of water and distribute it between three test-tubes. To one test-tube add a drop or two of mercurous nitrate solution (?), to the second a drop of lead nitrate solution (?), and to the third a drop of silver nitrate solution (?). After allowing the contents of each tube to settle, pour away the liquid, add water, and boil (?). Allow to cool, and note, by the appearance of crystals, which of the precipitates is soluble in hot water.

These precipitates are given, not only by hydrochloric acid, but by any chloride, and are, therefore, means of recognizing the presence of the chloride radical which is common to all chlorides.

33. Theory of the Method Used in Preparing Hydrogen Chloride. To a concentrated solution of sodium-hydrogen sulphate add pure concentrated hydrochloric acid (?). Add the acid a very little at a time to avoid over-rapid precipitation, and agitate between additions. The longer the operation takes, the better. Examine the result with a lens (?).

Write the equation for this action. What relation does this action bear to that in **31** *c*? What circumstances determine the direction of a reversible action [R 180]?

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CHAPTER VII.

EQUIVALENT WEIGHTS, FORMULÆ, EQUATIONS.

34. Composition of Carbon Dioxide [Quant. Two students working together]. Fit a piece of hard glass tubing, 25–30 cm. long, with perforated corks. Insert at one end a short piece of glass tubing and at the other a U-tube, as in Fig. 12. The

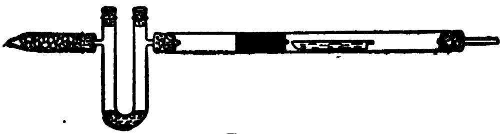

Fig. 12

inner edges of the hard glass tube should be rounded with a file, or flared by use of the blast-lamp and a piece of charcoal. Rubber stoppers will give tight joints more surely than corks. Attach to the U-tube by means of a cork a short, straight tube, of the diameter of a narrow test-tube, which has been drawn out [Bunsen flame] so as to leave a small opening at the free end. Arrange a loop of thread [Side-shelf] with which to suspend the U-tube from the balance. Place in the hard glass tube a plug of granular cupric oxide, about 4 cm. in length. This may be held in position by small wads of asbestos. The cupric oxide and asbestos must be dried by heating in the porcelain crucible before use. Put about 0.2 g. of pure dry sugar-charcoal [Instructor] in a porcelain boat, weigh the boat with contents, and set it in the tube close behind the cupric oxide. Make a few c.c. of a strong (approximately 30 per cent) solution of potassium hydroxide, fill the bend of the U-tube with it, and charge the small tube beyond with fragments of solid caustic potash. Test the apparatus with the greatest care to see that it is absolutely air-tight [Instructions]. Finally, immediately before starting the combustion, weigh the connected potash tubes, replace them in position, and test once more for air-tightness.

Slip a cylinder, made by rolling a piece of wire gauze, over the hard glass tube, connect the latter with the oxygen cylinder (or other source of oxygen), and heat the part containing

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the boat and cupric oxide with two burners (extra Bunsen burner from storeroom). Turn on the oxygen with care and regulate the stream so that the carbon may burn slowly and not more than 15–20 bubbles of unused oxygen escape per minute. A more rapid stream will involve the loss of carbon dioxide. Heat the front of the boat first and let the glow, caused by the combustion, travel along. The burning will take 30–45 minutes. Continue the stream of oxygen for 4–5 minutes after the carbon is completely burned (why?), then disconnect the potash apparatus and weigh it. A more accurate result is obtained by finally displacing the oxygen by air (why?). After the tube has cooled, weigh the boat with any ash it may contain. Return the cupric oxide to the bottle.

The loss in weight of the boat gives the amount of carbon; the gain in weight of the potash apparatus, the amount of the carbon dioxide. The difference of these two gives the oxygen.

Calculate from your data the weight of carbon combining with 8 parts of oxygen.

$$\text{Wt. of ox. found : Wt. of carbon found : : } 8 : x.$$

This gives x, the combining weight [R 46] of carbon. This weight of carbon is equivalent [R 49] to those amounts of other elements which likewise unite with 8 parts of oxygen.

Assuming the atomic weights of carbon and oxygen to be 12 and 16 respectively, calculate from your data the formula of carbon dioxide [R 57].

Make the equation representing the action.

35. Composition of an Oxide of a Metal [Quant. Note 22, p. 7]. On account of the difficulties attending the making, the collecting, or the weighing of most oxides formed by direct union, the following indirect method is suggested. It consists in converting a known weight of a metal into the nitrate of the metal by the action of nitric acid, and obtaining the oxide by decomposition of this salt. Attempt no equations for these actions.

a. Composition of an oxide of iron. Weigh an evaporating-dish of medium size, place in it about 1 g. (12 inches) of pure iron wire, and weigh again. Cover the dish with a watch-glass, convex side downward, and add 10 c.c. of pure dilute nitric acid. Set the dish, covered, on the water bath until the iron has dissolved, adding a few drops of concentrated nitric acid if any of the wire remains unattacked [Instructions]. Then rinse the cover-glass carefully into the dish and remove it, and evaporate the solution to dryness on the water bath or on a

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beaker of boiling water [Hood]. When the residue (what is it?) is dry, place the dish on a clay triangle supported on the ring-stand and heat carefully with a burner held in the hand as long as any red fumes are given off. During this process, and especially at first, great care and patience must be exercised, as too rapid heating may cause solid particles of the product to be thrown from the vessel. If any crackling noise is observed, remove the burner at once. When, after final strong heating of every part of the material, red fumes or other evidence of continued change can no longer be perceived, allow the dish and contents (?) to cool and weigh them. To make sure that the decomposition was complete, heat once more, cool, and weigh again. This precaution is always necessary in experiments of this nature.

The difference of the weights of the metal and of the oxide gives the weight of oxygen combined with the known weight of iron.

Calculate from your data the weight of iron (x) combining with 8 parts of oxygen.

$$\text{Wt. of ox. found} : \text{Wt. of iron} :: 8 : x.$$

This is the combining weight [R 46] of iron in this oxide. This weight of iron is equivalent [R 49] to those amounts of other elements which likewise unite with 8 parts of oxygen.

Assuming the atomic weights of iron and of oxygen to be 55.9 and 16, respectively, calculate from your data the formula of the oxide of iron [R 57]. What is the name of this oxide? What other oxides of iron are known [R]?

b. Pure zinc (about 1 g.) may be used instead of iron. The manipulation is the same as in **35** *a*. The residue from evaporation is a syrup-like body, however, which cannot be dried. Extra caution must, therefore, be used in heating this to avoid loss by spirting.

Calculate the combining (equivalent) weight of zinc and the formula of the oxide as in **35** *a*.

c. Magnesium wire (about 1 g.) may be used instead of zinc (**35** *b*). Equal care is required during the evaporation and heating. Tin (about 1 g.) may also be used.

36. Equivalent Weight of a Metal by Displacing Hydrogen [Quant.].

a. First fill the pneumatic trough and 1-liter bottle with water so that the liquid may acquire the temperature of the room. Fit a 100 c.c. flask somewhat as in Fig. 8, using in place of the thistle-tube a dropping-funnel (see **36** *b*). To carry a doubly-bored cork the mouth of the flask must be rather wide.

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A larger flask than 100 c.c. must not be employed on account of the waste of acid its use would entail. The stem of the dropping-funnel must reach to the bottom of the flask, and the inner end of the L-tube must not project below the bottom of the cork. Attach a rubber or glass delivery tube and see that the apparatus is air-tight. Weigh a piece of chemically pure zinc, taking about 2 g. Without detaching your platinum wire from the glass rod, wrap it tightly round the zinc (why)? and allow the whole to slide gently into the flask. Fill the apparatus completely, from the top of the stem of the funnel to the tip of the delivery tube, with water. Close the stopcock when the bulb has almost emptied itself. Invert the 1-liter bottle, filled with water, on the shelf of the pneumatic trough, and put the delivery tube in position.

Fill the globe of the funnel with pure concentrated hydrochloric acid [Side-shelf] and admit this to the flask, a little at a time, in such a way that a steady, but not too violent, action takes place. A good deal will be needed at first before sufficiently rapid action begins (why?). When the metal is entirely dissolved, drive all the gas over into the bottle by pouring water once more through the funnel (be careful that no air is carried over with the water).

The weight of the hydrogen which has been displaced by the weighed quantity of zinc is to be ascertained in this experiment, not by direct weighing, but, as follows, by measuring the volume of the gas and calculating its weight from this and the density of hydrogen:

When the gas has acquired the temperature of the water and room, lower the bottle until the level of the water outside and inside is the same. If there is still a good deal of water in the bottle, the latter may have to be inclined to accomplish this and the following operation. Close the bottle with a cork while it is in this position and remove it from the trough. To find the volume of the gas, weigh (to the nearest gram) the bottle as it stands on the laboratory scales, and also completely filled with water, and subtract. Since 1 c.c. of water weighs approximately 1 g. the number of grams in this difference gives at once the number of c.c. of hydrogen. Why is this method of measuring the volume of the water more accurate than using the graduated cylinder? Record the temperature of the hydrogen by reading a thermometer hung in the laboratory close to the apparatus. Read the barometer, and record the corrected reading [Note 31, p. 18]. Since the hydrogen is mixed with water vapor, correct for the latter by subtracting the aqueous tension (Appendix II) at the observed laboratory temperature

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from the corrected barometric reading. This gives the true partial pressure of the hydrogen.

Reduce the volume of the hydrogen, by rule, from the observed temperature and partial pressure to 0° and 760 mm. Find by calculation (1 liter weighs 0.09 gr. at 0° and 760 mm.) the weight of the hydrogen obtained. Calculate the equivalent weight of zinc, i.e., the weight of the metal (x) which displaces 1.008 g. of hydrogen:

$$\text{Wt. of hyd.} : \text{Wt. of zinc} :: 1.008 : x.$$

Calculate from the result how many equivalent weights of hydrogen would be displaced by 65.4 g., the gram-atomic weight, of zinc. What is the valence of zinc? How many formula-weights of hydrogen chloride are required to furnish the hydrogen displaceable by one atomic weight of zinc? Write the left-hand side of the equation in accordance with this result.

Wash the trough carefully until it is absolutely free from acid, and put it away in an inverted position to avoid rusting.

b. The above experiment may be performed with magnesium (about 0.9 g.), iron (about 1. 8 g.), or aluminium (about 0.8 g.) in place of zinc.

In the absence of a dropping-funnel, a substitute may be made by connecting a funnel with a straight tube by means of a rubber joint closed with a pinch clamp. Or, the aspirator (Fig. 7) may be used here, the metal (half the above quantities), water, and a smaller tube containing the acid being placed in the test-tube, and the mixing being effected by inclining the bottle after the apparatus is connected.

37. Inter-Equivalence of Equivalent Weights (Law of Reciprocal Proportions). If **35** *b* was performed, compare the quantity of zinc which combined with 8 g. of oxygen with that which in **36** *a* was found to displace 1.008 g. of hydrogen. If they are identical, these two quantities of oxygen and hydrogen are chemically equivalent and may combine with one another. What substance has precisely this composition?

If magnesium was used, in **36** *b*, compare the quantity with that combining, in **35** *c*, with 8 g. of oxygen and answer the same question.

38. Combining Weights of Zinc and Chlorine [Quant.]. (From Torrey's *Elementary Studies.*) Weigh an evaporating-dish of medium size and place in it about 2 g. of pure zinc. Add a little diluted (1 Aq.: 2 acid), pure, concentrated hydrochloric acid [Side-shelf] and cover with a watch-glass, convex side downward. If the action is very slow, the tip of a platinum

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wire may be placed in contact with the zinc. Maintain a brisk action by further additions of concentrated hydrochloric acid in very small amounts at a time. Final excess of the acid should be avoided, as time will be lost in the subsequent evaporation. When the metal is completely dissolved, rinse the cover-glass and platinum wire carefully into the porcelain dish and remove them. Allow the solution to evaporate as far as possible on the water bath or on a beaker of boiling water [Hood]. Now place the dish on the ring-stand, and, using a small Bunsen flame, allow the syrup-like solution to evaporate slowly to dryness. Then heat the white mass to the point at which it has completely melted and no further. The best way to achieve this with the minimum rise in temperature is to let the Bunsen flame play on the surface from above. Overheating must be avoided, because the product is volatile at high temperatures. The moment the dish has so far cooled that the hand can be borne upon the bottom, wipe the dish carefully and weigh it. The substance absorbs moisture greedily from the atmosphere, hence expedition is required in cooling and weighing if accurate results are to be obtained. To insure accuracy, the melting, cooling, and weighing should be repeated, and the lower result taken as correct.

Calculate, from the data obtained in this experiment, how much chlorine combines with the equivalent weight of zinc found in **36** *a*. This amount is the equivalent weight of chlorine (x):

$$\text{Wt. of zinc} : \text{Wt. of chlor.} :: \text{Equiv. of zinc} : x.$$

Assuming the atomic weights of zinc and chlorine to be 65.4 and 35.45 respectively, determine the formula of zinc chloride.

Express the whole action of hydrochloric acid on zinc in symbols by making the equation in accordance with these conclusions. Which of the factors in the equation have you determined experimentally, and which not? What law do we use in assuming that the undetermined factors are correct?

39. Combining Weights of Lead or Silver and Chlorine. From the weights of lead (**9** *a*) or silver (**9** *b*) and chlorine found to combine, calculate the formula of lead (or silver) chloride.

40. Multiple Proportions [Quant.].

a. [Two students working together]. Fit a hard glass tube with corks through which pass short pieces of narrow glass tubing (Fig. 9). Fix the tube in a clamp upon the ring-stand, attaching the clamp close to one end so that the rubber covering of the clamp may be away from the central part which is to

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be heated. Make sure that the apparatus is air-tight. Dry some pulverized cupric oxide by heating it in a hard glass test-tube. Weigh two clean, dry, porcelain boats, and place in one about 1.5 g. of the cupric oxide and in the other 2.5 g. or more of cuprous oxide * [From Instructor] and weigh each again. In recording the weights and in handling the boats be careful to distinguish the one from the other. Place the boats in the hard glass tube, so that the points of the boats touch in the center of the tube. Connect the end nearest to the cuprous oxide with a source of dry hydrogen (Kipp's apparatus and drying-bottle, or laboratory supply).

Pass a gentle stream of hydrogen through the apparatus until a test (?) shows that the air has all been displaced. Reduce (why?) the speed of the gas until the bubbles in the washing-bottle can easily be counted. Now heat the boats moderately, beginning with that containing the cuprous oxide. What collects in the cooler end of the tube? Where does it come from? When the action, which requires 10–15 minutes, is finished, allow the boats to cool in a stream of hydrogen. Weigh the boats and contents (?), taking care not to interchange them. To ascertain whether the action is complete, heat the boats once more in hydrogen, cool, and weigh again.

Determine by difference the weights of oxygen and copper in each case, and calculate from the data how much copper is combined with 8 parts of oxygen in each of the two oxides. What is the ratio of the two values of copper? Show that the result illustrates the law of multiple proportions.

Assuming 16 and 63.6 to be the atomic weights of oxygen and of copper, respectively, calculate from the data the formula of each oxide. Construct the equations representing the action of hydrogen upon each oxide.

b. Pure lead dioxide and pure lead monoxide may be used as in *a*, if available. The monoxide, however, absorbs carbon dioxide readily from the air, and therefore does not keep well. The experiment must, therefore, be tried by the instructor before the material on hand is given to the class. Lead monoxide is more difficult to reduce than the dioxide. The heating in a stream of hydrogen must be repeated to constant weight.

c. If the quantitative decomposition of potassium chlorate (15 *b*) was carried out, dried potassium perchlorate may be decomposed in the same way and the results compared. Weigh an open, long, hard glass test-tube. Place in it about 1 g. of

* Pure cuprous oxide (Kahlbaum's) can be kept successfully if sealed up in small bottles which are not opened until needed.

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potassium perchlorate and weigh again. Then heat the tube and drive off the oxygen slowly, and weigh again. Heat strongly once more, to constant weight. Ascertain by difference the weights of potassium chloride (residue) and of oxygen.

The formula of the perchlorate is $KClO_{x'}$. Calculate from your data how much oxygen ($O_{x'}$) is combined with 74.6 g., the formula-weight, of potassium chloride (KCl). This result, the formula-weight of the oxygen, will be a multiple of 16. Compare this formula-weight of oxygen with that found in the experiment with potassium chlorate, and show how the results illustrate the law of multiple proportions. Find the formula of potassium perchlorate and write the equation for the decomposition of the compound.

41. Dulong and Petit's Law. According to Dulong and Petit [R 211], if the correct atomic weight, when it has been found, is multiplied by the specific heat of the element in the solid form, the product is a number which in most cases lies between 6 and 6.8.

Take the values of such combining weights or equivalents as you have found experimentally, viz., iron (**35** *a*, **36** *b*), zinc (**35** *b*, **36** *a*), magnesium (**35** *c*, **36** *b*), aluminium (**36** *b*), silver (**39**), copper (**40** *a*, two values), or lead (**39**, one value, and **40** *b*, two values), and multiply each by the corresponding specific heat (Appendix III). If the result is about 6.4, the atomic weight is the same as the equivalent weight. If not, multiply the equivalent weight by the smallest integer which will bring the final product within the limits 6 to 6.8. The integer used is the valence of the element, and the product of the equivalent weight and the valence is the atomic weight. Show the working in your notes and give a list of the atomic weights and valences found. In the case of copper or lead, distinguish the valences in the two compounds.

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CHAPTER VIII.

BROMINE, IODINE, FLUORINE, AND THEIR COMPOUNDS WITH HYDROGEN.

CHLORINE (Chap. VI) and the elements to be studied in this chapter form a group having very similar properties, and are called the halogens. Recall the facts about chlorine and hydrogen chloride, and use them as a guide in trying to understand the chemistry of the rest of the group. Remember particularly that chlorine is colored, has a powerful odor, and does not cause fumes in moist air; and that hydrogen chloride is colorless, and causes dense fumes in moist air. The corresponding substances throughout the group may be expected to present properties like these. Thus, the elements are all colored substances, the hydrogen compounds are all colorless and fume in moist air. The hydrogen compounds, hydrogen chloride, hydrogen bromide, etc., are known as the hydrogen halides.

42. Preparation of Bromine [Hood]. Powder about 1 g. of potassium bromide, mix it in the mortar intimately with about 2 g. of pulverized manganese dioxide, and place the mixture in a test-tube. In a second test-tube dilute 2–3 c.c. of concentrated sulphuric acid [Desk] with half its volume of water (add the acid, cautiously, to the water), and mix with the contents of the first test-tube enough of this solution to moisten the materials thoroughly, and no more. After allowing the mass to stand for a few minutes, apply a gentle heat to the tube, and note the color and behavior of the vapors evolved (?). Apply a strip of filter paper moistened with a starch-potassium iodide emulsion (**29** *a*) to the mouth of the tube (?).

What other materials might be substituted for the potassium bromide in the above experiment?

43. Properties of Bromine.

Shake up one drop of bromine [CARE. Do not spill upon the hands] with 10 to 15 c.c. of water in a test-tube, and divide the solution ("bromine-water") between four test-tubes.

a. To one of these add 1–2 c.c. of ether, and shake (?). Note the relative solubility of bromine in ether and in water as displayed by the depth of color in each layer (**26** *g*). To the second add carbon disulphide (?), and to the third chloroform (?), observing as before. To about 10 c.c. of starch

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emulsion add a few drops from the fourth test-tube (?) [R 230 and see result of **47** *b*, below].

b. Fit up an apparatus to generate a small amount of chlorine [Hood], using a side-neck test-tube instead of the flask in Fig. 11 (p. 29). If chlorine-water is available, it may be used instead of the gas.

Dissolve a single, very small crystal of potassium bromide in a few c.c. of water in a test-tube. Add several drops of carbon disulphide, and then pass a few bubbles of chlorine through the solution, or add a few c.c. of chlorine-water (?). Shake, and notice the appearance of color in the carbon disulphide (?). Infer from this result the relative activities of chlorine and bromine (?). The result measures the relative affinity of chlorine and bromine for what elements?

The chlorine generator, if used, is required again in **47** *c*, which may be performed at once, before the apparatus is taken apart and cleaned. Prepare also 5 c.c. of saturated chlorine-water, if not furnished on the side-shelf, cork it up in a test-tube, and set it aside in a dark place for use in **45** *g* and **50** *a*.

44. Preparation of Hydrogen Bromide.

a. Pulverize about 1 g. of potassium bromide, place it in a test-tube, and cover with concentrated phosphoric acid solution. Notice the apparent slowness of the action on account of the insolubility (physical) of the compound in the liquid (sodium bromide is much more soluble, and should be used, if available). Warm, if necessary. Observe the odor (?), and insert a rod dipped in ammonium hydroxide solution (?) [Note 33, p. 31].

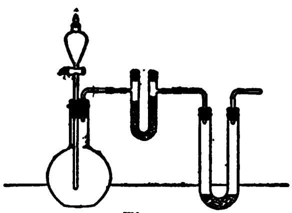

Fig. 13

For the action of sulphuric acid with a bromide, see **52** *b*.

b. Fit up a 250 c.c. flask with a dropping-funnel and exit tube, and connect with a U-tube (Fig. 13). Render the apparatus air-tight. Fill the U-tube with dry, broken glass or porcelain, mixed with a little red phosphorus (why?). Connect the other limb of the U-tube with a second, larger U-tube [Store-room] containing about 10 c.c. of water. Place about 5 g. of red phosphorus mixed with twice its weight of sand in the flask, add 5 c.c. of water, and mix by shaking. Pour into the globe of the funnel about 8 c.c. of bromine [Extreme care. Do not spill upon the hands (Note 16, p. 2)]. Allow the bromine to flow drop by drop on to the phosphorus, and

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let the gas dissolve in the water in the second U-tube. A large volume of air is expelled before the hydrogen bromide reaches the second U-tube. Disconnect the second U-tube and reserve the solution for use in **45.**

Try the effect of moist air upon the gas issuing from the main apparatus (?). Hold in the gas a rod dipped in ammonium hydroxide (?).

45. Properties of Aqueous Hydrobromic Acid. Divide the solution into seven portions and examine its behavior toward (*a*) litmus (?), (*b*) zinc in contact with a platinum wire (?), (*c*) silver nitrate solution (?), (*d*) mercurous nitrate solution (?), (*e*) lead nitrate solution (?), (*f*) powdered manganese dioxide (warm) (?). Boil *c*, *d*, and *e*, after pouring away the supernatant liquid and adding more water to each (?). Compare these results with those found in the case of hydrochloric acid (**32**).

g. To the seventh portion add a few drops of chlorine-water (**43** *b*), a few drops of carbon disulphide, and shake (?). This result indicates the relative affinities of chlorine and bromine for what elements, and how?

46. Preparation of Iodine. Prepare a mixture of potassium iodide (1 g.) and manganese dioxide (2 g.) exactly as in **42**, place it in an evaporating-dish, and moisten (2–3 drops) with sulphuric acid diluted with water (1 Aq.: 2 acid). Cover the dish with a watch-glass (partially filled with cold water to cool the surface presented to the vapors) and warm very gently. After a time examine the sublimate [Note 34, below]. Expose a strip of filter paper, moistened with starch emulsion alone, to the vapors (?). Recall the interaction of chlorides with manganese dioxide and sulphuric acid [R 172].

What other materials might be substituted for potassium iodide in preparing iodine?

Note 34. — Stains upon the fingers caused by iodine may be removed by rubbing with sodium thiosulphate solution ("hypo").

47. Properties of Iodine. Shake a few crystals of iodine vigorously [Note 34] with about 10 c.c. of water in a test-tube. Pour the clear liquid off, dividing it equally between four test-tubes.

a. Add to one portion a few drops of chloroform, to another ether, and to a third carbon disulphide. Shake each vigorously and note the relative solubility (estimated by depth of color) of iodine in water as compared with that in each of the other solvents (?).

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b. Take 15 c.c. of starch emulsion and add the fourth portion to it (?). Pour the mixture into the graduated cylinder and add water so long as a sample poured out into a test-tube continues to show an easily perceptible color. Why is the use of starch considered to be a delicate test for iodine? Does it show the presence of iodine in combination (**48** *b*)?

c. Repeat **43** *b*, using a very small crystal of potassium iodide (?). Infer the relative activities of chlorine and iodine. The result measures the relative affinities of these two halogens for what elements?

d. Repeat *c*, using potassium iodide, but substituting bromine-water for chlorine. In what order do the halogens stand, in respect to activity, and why do you place them in that order?

48. Preparation of Hydrogen Iodide [Hood].

a. Repeat **44** *a* with potassium iodide or sodium iodide (?).

b. Use the apparatus in Fig. 13. Place in the flask a mixture of finely powdered iodine (20 g.) and red phosphorus (3 g.) intimately mixed in the mortar. Charge the U-tubes as in **44** *b*. Place a little water in the dropping-funnel (or substitute, **36** *b*), warm the materials in the flask very slightly (Extreme caution!] by waving the Bunsen flame once or twice under the vessel, and allow the water to drop very slowly upon them (?). After the air has all been expelled, and the solution in the second U-tube has become sufficiently concentrated, remove the second U-tube. Test the issuing gas with moist air (?) and with ammonia (?) as in **44** *b*. Hold in the gas a piece of filter paper dipped in starch emulsion alone (?). Explain. Reserve the contents of the second U-tube for use in **50** *a*.

49. Preparation of Hydriodic Acid [Hood]. Place 5 g. of powdered iodine with 50 c.c. of water in a small flask provided with a cork and an L-tube extending to the bottom. Pass hydrogen sulphide from a Kipp's generator, or from the laboratory supply, through the mixture, loosening the cork once or twice at first to permit the air to be displaced by the gas, until the iodine is all gone and the solution no longer becomes brown on being shaken. Agitate constantly to hasten the process. Describe what happens. Warm and filter the solution.

Obtain a distilling-flask and condenser [Storeroom] and distil the filtrate fractionally (Fig. 14), collecting first the part that comes over at 100°, then the parts boiling between 100–103°, 103–106°, and so forth. Use a very small flame, and be careful not to allow it to reach the walls of the flask above the liquid, or breakage will take place. A large flame may not only crack

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the flask, but may also cause the thermometer to show a higher temperature than it could acquire from the vapor alone. Stop when the liquid is nearly all distilled off. Note the highest

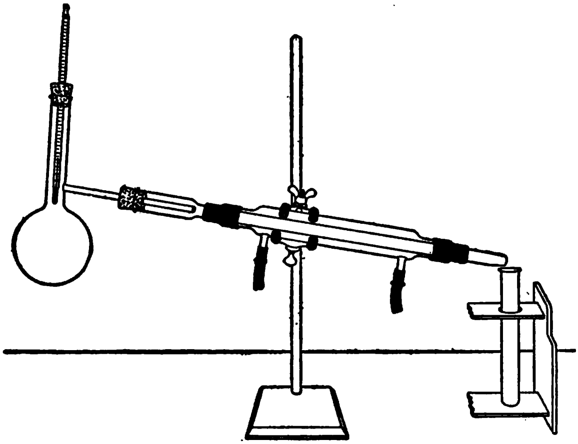

Fig. 14

temperature reached. Pour the residue into a test-tube and keep the series for use in **50** *b*.

What substance causes the color of the higher fractions and of the residue? Confirm your conclusion by a suitable test (**47**). How is this colored substance formed?

50. Properties of Hydriodic Acid.

a. If **48** *b* was done, carry out the same experiments with the solution as were made with the solution of hydrobromic acid in **45** (?). Compare the results with those of **45** (?).

b. If **49** was done, add silver nitrate solution to each of the fractions above 100° obtained in **49**, using only a part of the liquid in the case of the two with the highest boiling-points. At what temperature did the most concentrated solution of hydrogen iodide come over? What peculiarity of aqueous hydriodic acid does the result indicate? What other solutions show the same peculiarity [R 182, 232, 239, 241, 387, 440]?

Place a piece of zinc, in contact with a platinum wire, in the remainder of one of the higher fractions (?). Test the other with litmus paper (?), and then add pulverized manganese dioxide, and warm (?).

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51. Hydrogen Fluoride. Cover a square of glass with a thin layer of paraffin by warming it very cautiously far above a Bunsen flame and rubbing it on one side with solid paraffin. Moisten about 3 g. of fluorspar in a leaden dish [Storeroom] with concentrated sulphuric acid (do not cover with the acid). With the end of a file draw some design upon the paraffin-coated side, thus exposing parts of the glass to the action of the vapor. Now cover the leaden dish with the glass, paraffin side down, and set it in a moderately warm place, but not so warm that paraffin may be likely to melt. After half an hour or more remove the glass cover, warm, and wipe off the melted paraffin with filter paper (?). Write equations representing the action, and state what becomes of each of the constituents of the glass [R 243, 521]. Try the test of a rod dipped in ammonium hydroxide and held over the contents of the lead dish (?). Does the gas fume with moist air? What substances, beside fluorspar, would serve the purpose of this experiment? Why could not hydrochloric acid or nitric acid be substituted here for sulphuric acid? What acid that we have employed could be used here?

How may fluorine be liberated from a fluoride? Why can it not be isolated from fluorides by the action of oxidizing agents, as was the case with the other halogens?

52. Reducing Action of Hydrogen Iodide and Hydrogen Bromide [Hood]. In connection with this experiment, it must be kept in mind that an odor similar to that of rotten eggs shows the presence of hydrogen sulphide (**49**), and an odor of burning sulphur the presence of sulphur dioxide (**13** *a*).

a. Pulverize finely about 1 g. of potassium iodide, place it in a test-tube, and moisten with one or two drops of concentrated sulphuric acid (?). If too much acid has been taken, start again. Warm gently. Investigate the result, which furnishes a mixture of gases, as follows:

α. Breathe across the mouth of the test-tube to ascertain the effect of the gas on moist air (?). What gases previously made showed the same behavior? What do you infer in this case? To confirm this conclusion, lower a glass rod dipped in ammonium hydroxide into the test-tube (?).

β. Is any characteristically colored vapor (?) mixed with the gas recognized in *α*? Can you observe any other property which identifies the substance? By what kind of chemical action could this colored substance be formed from the product identified in *α*? By what name is such a reaction known? Was there any corresponding product formed when sulphuric acid acted upon a chloride?

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γ. Can you recognize still another (gaseous) product by its odor?

The work in α and β and γ leads to the recognition of three gaseous or vaporous products. Do not attempt to put all of these in one equation. Construct an equation for the formation from the original materials of the gas recognized in α (primary action), and make a separate equation for the formation of the other two products from the interaction of sulphuric acid with the gas recognized in α (secondary action). What two properties of sulphuric acid and what property of hydrogen iodide are illustrated by this set of observations?

In case the above directions are not followed implicitly, and large pieces of potassium iodide are taken, or too much sulphuric acid is used, still another gas (sulphur dioxide) may be formed along with or instead of one of the above, and, in addition, a sublimate of free sulphur may be seen on the tube [R 237].

b. Repeat the work in *a*, using powdered potassium bromide instead of the iodide, and answer the same questions.

53. Identification of Halogen Compounds. Imagine that there are given to you four white substances, and that you know them to be the fluoride, chloride, bromide, and iodide of some metal. State what experiments you would make, and what reasoning you would use, in order positively to identify the halogen constituents of each. In two of these cases, two different actions have been encountered in this chapter and might be used, and in the other two cases only one. Still another kind of action might readily be thought of [R 63, 311]. Negative results, say by showing that one is not a chloride, bromide, or iodide, and is therefore a fluoride, must be confirmed by a positive experimental test.

If the four hydrogen halides were given you in gaseous condition in four jars, how should you proceed by chemical means to identify each?

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CHAPTER IX.

DOUBLE DECOMPOSITION. OXYGEN COMPOUNDS OF THE HALOGENS. HYDROGEN PEROXIDE.

54. Radicals and Double Decomposition.

a. To a few drops of potassium chloride solution add silver nitrate solution (?). What kind of chemical interaction do salts usually show in solution [R 264. See Note 4, p. 1] ? Write the equation for this action. How can we tell whether the precipitate is silver chloride, or potassium nitrate, or both? Which is it (Appendix IV)? What was the interaction of silver nitrate with hydrochloric acid (**32** *g*)? To a few drops each of solutions of two other chlorides, such as ferric chloride and calcium chloride, add a little silver nitrate solution (?). To find out whether all substances containing chlorine give silver chloride in this way, try a few drops of potassium chlorate solution with the same silver compound (?). State now what radical a substance must contain in order that, with silver nitrate, it may yield silver chloride (?).

b. To a few drops of silver sulphate solution add a solution of any chloride (?). To find out whether all substances containing silver yield silver chloride in this way, take a few drops of silver nitrate solution in each of two test-tubes. To the one portion add some ammonium hydroxide, and so obtain a solution of ammonio-silver nitrate ($Ag(NH_3)_2NO_3$). To the other add some potassium cyanide solution [CAUTION! POISON!] until the liquid is clear [Note 35, below], and so obtain a solution of potassium argenticyanide ($KAg(CN)_2$). Now add to each of these a solution of sodium chloride (?). Is the silver radical present? Do all substances containing silver, when mixed with a chloride, give silver chloride? Which compounds alone give silver chloride by double decomposition?

c. Which substances alone will, by addition of mercurous nitrate, give mercurous bromide (**45** *d*)? Which substances alone will, by addition of silver nitrate, give silver iodide (**50** *a* and *b*)? Which substances alone will, by addition of an acid, give hydrogen chloride (**31**)? Name the classes of substances which are composed of radicals, and commonly interact by double decomposition.

Note **35.** — An insoluble body will not dissolve *as such* merely because of the addition of an excess of the precipitant, or even

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because of the introduction of a different reagent. When an insoluble body appears to go into solution, the phenomenon indicates that the substance added has interacted chemically with the insoluble substance and has produced a new substance which is soluble.

55. Chemical Equilibrium in Double Decomposition.

a. When solutions of two substances, each composed of two radicals, are mixed, and no precipitate is observed, interaction nevertheless occurs. Why was no precipitate observed when solutions of silver nitrate and potassium chlorate (**54** *a*) were mixed? To answer this question, write the equation for the double decomposition which might occur, and consider the solubilities of the products (Appendix IV). A similar case where the presence of the products is easily shown may now be studied (see *b*).

b. Place 10 c.c. of water in each of two test-tubes, add to one a single drop of ammonium thiocyanate solution, and to the other a single drop of ferric chloride solution. Now mix the solutions (?). Write the equation for the action which may be assumed to have occurred. Is there any evidence that interaction has taken place? Which of the four is the colored substance? Use the mixture for *c*.

c. When no precipitate is formed, is an action like the above (*a* or *b*) complete? To answer this question, divide the mixture from *b* equally between four test-tubes. Keep one for reference. To the second add one drop of ferric chloride solution (?), and to the third a drop of ammonium thiocyanate solution (?). Interpret the result. Now add to the fourth tube a few drops of ammonium chloride solution (?) and explain.

What other action have we shown to be reversible (**33**)? All double decompositions of substances composed of radicals are reversible, like these two. They are also often far from complete, when, as in the present instance, precipitation does not occur. Why does precipitation tend to make the action more nearly complete?

56. Hypochlorous Acid and Hypochlorites [Hood]. Fit up a chlorine apparatus (**29** *b*) capable of delivering a large amount of chlorine and make sure that it is air-tight. Use the same source of chlorine in **56** and **57**. Between experiments, immerse the end of the exit tube in sodium hydroxide solution, and allow none of the gas to escape into the room.

a. Make an aqueous solution of chlorine in a test-tube. Retain a few drops of this for use in *b*, and place in the remainder some litmus paper, paper with printing [R 476] and pen [R 754] and pencil [R 475] marks upon it, and a piece of

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colored calico. Observe the effect on each. Explain [R 176, 269].

b. To a few drops of chlorine-water add a drop of indigo solution [R 269] (?).

c. Place about 5 g. of quicklime in a small beaker, add a few c.c. of water, warm slightly, and allow to slake (?). Now add a little more water to make a thin paste, and pass chlorine into the mixture for 10–15 minutes (?), keeping the vessel cool by surrounding it with cold water (why?) and stirring the contents during the process. Filter the paste, with the addition of some water if necessary, and soak a piece of colored calico (?) and some litmus paper in the filtrate. Remove these articles to a beaker containing a little dilute sulphuric acid (?). Repeat these two operations with the same litmus and calico, if at first little effect is seen. What substance produces the effect? Why is the sulphuric acid required (see **55** *a*)?

What evidence does this experiment furnish that hypochlorous acid is a more active oxidizing agent than is atmospheric oxygen? Why is it thus more active?

How could you prepare an aqueous solution of pure calcium hypochlorite [R 267, 268]?

57. Chlorates [Hood].

a. Dissolve 3 g. (weighed on laboratory scales) of solid potassium hydroxide in 7 c.c. of water in a test-tube and saturate (Test? The solution must cease to feel soapy) the solution with chlorine. While the saturation is proceeding, calculate the volume of chlorine (at 0° and 760 mm.) required to interact with 3 g. of potassium hydroxide, one atomic weight of chlorine being needed for each molecule of potassium hydroxide. At five bubbles to 1 c.c., how many bubbles of chlorine will be used? Observe how many bubbles issue from your apparatus in fifteen seconds, and calculate how long the operation may be expected to take (?). Crystals will appear during the process of saturation and will increase in quantity as the liquid afterwards cools. Filter off the crystals on a small filter paper, and examine the filtrate and the crystals (in *b*) separately as follows:

Add to the filtrate dilute nitric acid (this is to destroy potassium hydroxide, in case any remains: no equation needed), and test with a few drops of silver nitrate solution (?). What radical is shown by this test to be present (**54** *a*)? What product is thus shown to have been formed by the interaction of chlorine and potassium hydroxide?

b. Examine the crystals from *a* with a lens and describe them. Dry the crystals, heat them in a narrow tube, and

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test for oxygen (?). Dissolve the residue from this operation in distilled water and add silver nitrate solution (?). What substances constituted the crystals and the residue, respectively? From the behavior of the former substance during making, what do you infer as to its solubility? Is the inference correct (Appendix IV)?

What effect was observed on adding silver nitrate solution to a solution of potassium chlorate (**54** *a*)? How may the chlorate radical be distinguished from that of the chlorides? The crystals of potassium chlorate made in *a* are not free from traces of potassium chloride (why?), and could not therefore be utilized for this test. What method should you suggest for purifying the chlorate [R 273]?

To a minute amount of finely powdered potassium chlorate add a few drops of pure, concentrated hydrochloric acid (**55** *a*) (?). The yellow substance is formed by decomposition of one of the products [R 275] (?). How would a chloride behave with hydrochloric acid?

Give the three ways of distinguishing chlorides from chlorates.

58. Perchlorates.

a. Measure 600 c.c. of water into your 1-liter bottle, and mark the level reached. Observe the temperature and pressure of the air and calculate the weight of potassium chlorate which will be necessary to give 600 c.c. of oxygen under these conditions (the tension of aqueous vapor may be neglected, as the vapor will occupy only about 10 c.c. of the 600 c.c. at 18°) and at the same time leave the perchlorate and chloride as a residue. This stage is reached when one-fifth of the total oxygen has been evolved: in other words, take so much of the chlorate as, if completely decomposed, would furnish five times 600 c.c.

Fill the 1-liter bottle with water and invert it over the pneumatic trough. Weigh the calculated amount of chlorate into a hard glass test-tube, which has previously been closely fitted with a one-hole cork and delivery tube, and see that the apparatus has been made air-tight. Gently heat the chlorate and collect in the 1-liter bottle enough oxygen to fill the bottle to the mark, measured, of course, when the mark is at the same level as the water in the trough. Proceed slowly towards the end so as to allow the gas to cool, stop heating when the mark is reached, and remove the delivery tube at once from the water. Pour the melted substance into a mortar before it has time to solidify. Pulverize the mixture.

The mixture consists mainly of the chloride and perchlorate

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of potassium. The solubilities (grams of the salt dissolved by 100 c.c. of water) of these salts are as follows:

	15°	20°	100°
Potassium chloride	33	35	56
Potassium perchlorate . . .	1.5	1.8	20

To separate the substances, calculate approximately the amount of potassium chloride which must be present, and shake the powder persistently with an amount of cold water just sufficient to dissolve this salt. Cut, fold, and place in a funnel a filter paper just large enough to hold the undissolved material. Collect the latter upon the filter and wash it with a few drops of cold water. Calculate the amount of water which at 100° will dissolve the residue, assuming it to be potassium perchlorate. Dissolve it in this amount of water by boiling, and allow the solution to stand for an hour or two. Collect the crystals upon a filter, wash them as before, and dry them on a radiator.

b. Dissolve a little of the substance in distilled water and test with silver nitrate solution (?). Explain (**55** *a*).

To a minute amount of the crystals add a few drops of pure concentrated hydrochloric acid [R 276] (?). Why does the result differ from that when potassium chlorate was treated with the same acid (**57** *b*)?

Place about 1 g. of the crystals in a narrow test-tube, heat, and test for oxygen (?).

How could you distinguish a perchlorate from a chloride, and from a chlorate?

59. Bromic and Iodic Acids.

a. Take two test-tubes and place in one a minute fragment of iodine and in the other 2–3 drops of bromine-water. Add about 5–10 c.c. of water and a little carbon disulphide to each, and shake (**43** *a* and **47** *a*). The carbon disulphide is added simply for the purpose of collecting the halogen and making its presence obvious. Now pass chlorine (generated as in **43** *b*), a few bubbles at a time, through (or add chlorine-water, a few drops at a time, to) the water in the test-tubes, alternately, and shake vigorously after each addition of chlorine until a change is seen [R 277] (?). Which of the halogens is first affected, and why?

b. To about 10 c.c. of water in a test-tube add a single drop of potassium iodide solution and then a single drop of potassium bromide solution. Introduce also a few drops of carbon disulphide. Now pass chlorine (generated as in **43** *b*), a few bubbles at a time, into the liquid, or add chlorine-water a

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little at a time, shaking vigorously after each addition of chlorine (?). Continue until no further changes occur, and explain all the changes which are observed. This procedure is used in analysis for recognizing a bromide in presence of an iodide.

c. Prepare some dilute bromic acid by taking 2–3 c.c. of potassium bromate solution and adding an equal volume of dilute sulphuric acid (?). Make the equation for this double decomposition. Is the action complete (**55**)? In what follows, disregard the substances present with the bromic acid, and place the latter only in the equation. Drop into this solution a single small crystal of iodine and shake repeatedly, allowing the mixture to stand for some minutes after each shaking(?). Pour off the solution from any undissolved iodine, and to the clear liquid add a few drops of carbon disulphide (?). What free halogen is here detected? What does this show in regard to the relative tendencies of bromine and iodine to unite with oxygen? What inference can you draw in regard to the relative activity of chlorine towards oxygen? What would be the action of iodine upon a solution of chloric acid?

Which variety of chemical change was here observed? How could you show that, although no change is visible, the bromic acid actually is formed when the sulphuric acid is added, above, and that it is the bromic acid, and not the potassium bromate, which interacts with the iodine?

60. Peroxides.

a. Dissolve about 2 g. of sodium peroxide in 100 c.c. of cold water in a flask. Add this amount of the oxide, a very little at a time, shaking and cooling (why? [R 571]) the mixture in a stream of water during the process. While still cooling the solution, add to it dilute sulphuric acid a few drops at a time until the mixture is acid (test?). What does the liquid now contain (**55** *a*)? Divide the mixture into four parts and use them in *b*, *c*, *d*, and *e*.

b. To one portion, contained in a small test-tube, add finely powdered manganese dioxide (?). Test the escaping gas for oxygen. What rôle does the manganese dioxide play here?

c. Prepare a solution containing free permanganic acid and sulphuric acid by adding a large excess of dilute sulphuric acid to 5 c.c. of potassium permanganate solution (equation? See **55**). Add some of this mixture to the second portion (from *a*). Test for oxygen the gas which comes off (?). What variety of chemical activity does the hydrogen peroxide show here?

d. To the third portion add some starch emulsion containing

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a drop of potassium iodide solution (?). In writing the equation for this action remember that the solution of hydrogen peroxide from *a* contained excess of sulphuric acid, which will interact (**55**) with the potassium iodide (?). The product of this action then interacts with the hydrogen peroxide. What variety of chemical activity does the hydrogen peroxide show here?

e. To the fourth portion add 5 c.c. of ether (object of this [R 306]?) and shake, and then add one drop and no more of potassium dichromate solution and shake again (?). This is one of the most characteristic and delicate tests for hydrogen peroxide.

State what substance here combines with the hydrogen peroxide and how it is formed [R 305–306]. Make no equation.

f. Suspend lead dioxide, barium dioxide, and pulverized manganese dioxide, separately, in water, add dilute sulphuric acid and shake for some time, cooling as in *a*. Filter, and apply to each filtrate the test described in *e* (?). What are the differences in behavior and constitution between a true peroxide and those oxides which are sometimes called peroxides [R 308]?

g. What are the radicals of: Bromic acid, potassium chlorate, hypochlorous acid, bleaching powder, sodium peroxide, potassium permanganate, iodic acid, potassium perchlorate?

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CHAPTER X.

IONIZATION AND INTERACTIONS OF ACIDS, BASES, AND SALTS.

61. Ionization. Name the four distinct methods by which we may ascertain experimentally whether a substance is ionized in solution or not, and learn the extent of the ionization [R 289, 292, 293, 328]. Define the term ionization.

The degrees to which aqueous solutions of many substances are ionized are given in Appendix VI. Constant reference to this will be necessary in interpreting the observations in this and succeeding chapters.

The experiments of this paragraph may be postponed until after the work in **62** or **63** has been done, if a set of the apparatus is not available at this moment.

Obtain [Storeroom] a pair of electrolytic cells* (Fig. 15) and

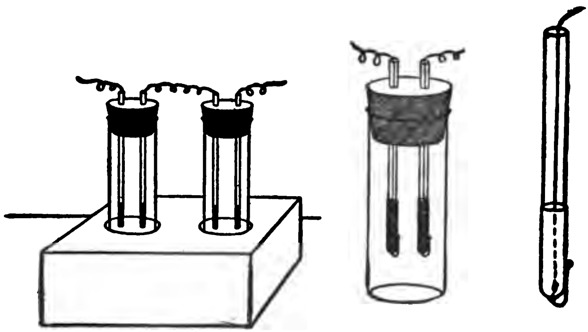

Fig. 15

half fill one with dilute sulphuric acid. When some material has been placed in the second cell, and both cells are connected

* Each cell consists of a glass, flat-bottomed, specimen tube (about 75 × 22 mm.) fitted with a two-hole rubber stopper in which a vertical groove has been cut to permit the escape of gases. The electrodes are pieces of glass tubing (about 10 cm. long) into which platinum wires have been sealed by means of sealing-glass. Contact is made by means of a thin copper wire welded to the inner end of the platinum wire. The platinum wire projects about 15 mm. and is turned upward and stuck to the outside wall of its tube by means of sealing-glass. To

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in series with the source of electricity,* an evolution of gas in the first cell will indicate that the circuit is complete and that, therefore, the material which has been placed in the second cell is a conductor. If, on the other hand, the material in the second cell is a non-conductor, or even a very bad conductor, no evolution of gas will be observed in the first cell. If the material in the second cell is a solution and a conductor, what conclusion may be drawn in regard to the condition of the dissolved body [R 326]?

Half fill the second cell with the substances named below in turn. See very particularly that the electrodes in each cell are not touching one another. Connect with the battery, and observe the effect in the first cell. When the same experiment has been shown in the class-room, the result may be recorded here and the experiment omitted. Wash the second cell and electrodes very carefully after each trial.

The following eight substances, or solutions, show the behavior typical of the classes of materials to which each example belongs. After giving the result in your notes, name the class which is illustrated in each case.

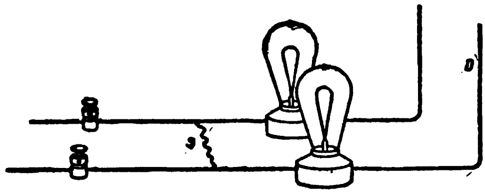

Fig. 16

secure a large electrolytic surface, the tubes are dipped for a distance of 20 mm. in strong chloroplatinic acid solution and heated in the Bunsen flame. This leaves a coating of metallic platinum on their surface.

The cells are set into holes bored in a small block of wood. To protect the latter from the action of acids the blocks should be prepared by soaking in hot paraffin.

* A storage battery of three cells in series may be used, but is always in danger of being ruined by short-circuiting through carelessness. Protection by means of a fuse leads to continual interruptions of the work. The best plan is to use the current passing from the lighting circuit (*D*, Fig. 16), through two 100-candle-power lamps (or an equivalent arrangement of other lamps), one on each wire from the dynamo, and to reduce the voltage to 6-8 volts by means of a suitable shunt (S). With a lamp on only one wire, there is danger that a student may produce a short circuit by allowing the other wire to touch a gas connection or steam pipe.

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a. Dry, crystallized sodium chloride (?).
b. Distilled water (?).
c. Aqueous solution of sodium chloride [Side-shelf] (?).
d. Diluted aqueous solution of sodium hydroxide [Desk] (?).
e. Diluted aqueous solution of hydrogen chloride [Desk] (?).
f. Aqueous solution of sugar (?). Dry the cell by washing first with alcohol and then with ether.
g. Toluene in the dried cell (?).
h. Hydrogen chloride dissolved in dry toluene [Side-shelf] (?). What difference between water and toluene do *e* and *h* bring to light? Keep this solution corked up in a dry test-tube for use in **65** *d*.

62. Ionic Materials. The chemical composition of the ions into which any compound is divided by solution in water may be ascertained in two ways: (1) by electrolysis and examination of the substances liberated at the electrodes [R 310–312], and (2) by studying the interactions (particularly the double decompositions, **54**) of the substance with other substances [R 281–283], for the radicals and ions of a substance are the same. What classes of chemical compounds are alone ionized?

The ionic substances may be named as follows:

Substance.	Name.
Ionic sodium ($Na^{\cdot}$)	Sodium-ion.
Ionic hydrogen ($H^{\cdot}$)	Hydrogen-ion.
Ionic chlorine (Cl')	Chloride-ion.
Ionic chlorate radical (ClO_3')	Chlorate-ion.
Ionic hydroxyl (OH')	Hydroxide-ion.
Ionic ferric iron ($Fe^{\cdot\cdot\cdot}$)	Ferric-ion.
Ionic ferrous iron ($Fe^{\cdot\cdot}$)	Ferrous-ion.
Ionic bisulphate radical (HSO_4')	Hydrogen-sulphate-ion.

In using these terms, note that sodium-ion (with the hyphen) is the name of the *substance*, and not of the hypothetical, charged atom. When speaking in terms of hypothesis, therefore, we may not say "a sodium-ion," or "sodium-ions," any more than we should say "an ionic sodium" or "ionic sodiums." To describe the charged atom or group of atoms, we must write "a sodium ion," "sodium ions," "chlorate ions," etc.

In accordance with the above nomenclature, give the names and symbols (not forgetting the charges) of the three chief physical components, i.e., distinct substances (in addition to water), present in the aqueous solutions of sodium chloride, hydrogen chloride, and sodium hydroxide [R 334] (?). In

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these solutions there are still other physical components present in small amounts — which are these in each of the cases just mentioned [R 344]? Give a concise comparative statement of the specific physical properties (such as, color, molecular weight, solubility, behavior towards electrically charged bodies, physical state) of the ionic and the free forms of sodium, hydrogen, and chlorine (?).

63. Relations of the Molecular Substance to its Constituent Ionic Substances (in Equilibrium). The ions of an ionogen and the remaining molecules are in chemical equilibrium [R 297]. What changes take place, respectively, when the solution is concentrated by evaporation and when it is diluted, as in *a*, below [R 297–298, 335]? Can the proportion of molecules be increased otherwise than by concentrating the solution (see *b*, below) [R 335–336]? With substances like sodium chloride and hydrogen chloride these changes cannot be perceived by the eye (why?). In the following instances (*a* and *b*) the ionic and molecular substances are both perceptible to the eye, and their relations as described above may, therefore, be studied very easily.

a. Examine a solution of potassium bromide. What is the color of bromide-ion? Take a minute amount (say 0.2 g.) of cupric bromide in a dry test-tube. Add two drops of water and agitate for some time (?). Then add more water, a drop or two at a time, agitating vigorously, and giving the substance time to dissolve, if it can, after each addition. Continue the addition of water cautiously until the substance has all dissolved, and afterward until the change in color is complete, and then stop. What is the color of the molecules of cupric bromide? What is the color of cupric-ion? Compare the color with that of cupric sulphate solution (?) and explain. Formulate the change which has been witnessed.

b. Now take a fresh portion of cupric bromide and repeat the experiment as in *a*, stopping the addition of water at the green stage. Divide the mixture into two parts. To one add 2–3 g. of solid potassium bromide and shake vigorously (?). To the other portion add 4–5 g. of solid cupric chloride (?). Interpret the results.

The converse case, in which one of the ions is removed and the dissociation is promoted, is discussed in *d*.

c. Many ionic substances are colored, although the color does not always differ markedly from that of the molecules. Examine the following solutions [Side-shelf], make a list of the ionic substances contained in them, with their formulæ and charges, and note the color of each kind of ions: cobalt chloride,

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potassium permanganate, potassium dichromate, chrome-alum (this last solution freshly made by dissolving the solid).

d. Just as the union of ions to form molecules may be promoted by addition of a substance yielding a common ion (? **63** *b*), so the reverse of this, namely, the dissociation of molecules into ions, may be promoted by the removal of one of the ionic materials. The removal of ions may be accomplished in several ways [R 360–364]:

(1) By union of the ion with some other ion, when the molecules thus formed are insoluble. This case will be illustrated next (see **64**).

(2) By union of the ion with some other ion, when the molecules thus formed, although soluble, are very little dissociated by water (see **66**, **75**, and **92** *a*).

(3) By discharge of the ion and liberation of its material, through transfer of the charge to another substance (see **68**).

(4) By union of the ion with some other material to form a compound ion, illustrated in **54** *b*.

(5) By decomposition of the ion, as in **59** *c*.

(6) By the mere change in the valence (amount of the charge) of an ion, for this converts it into another substance of the same material composition (see **160** *g*, **167** *b*, **168** *d*).

(7) By discharge of the ion and liberation of its material through electrolysis. This was illustrated in **61**.

64. Precipitation on Mixing Ionogens.

a. Place 3–4 c.c. of silver nitrate solution in a test-tube and dilute with water. Add potassium chloride solution cautiously and agitate continuously, until no further precipitation occurs (?). Filter, concentrate the filtrate by evaporation, and pour it into a watch-glass to crystallize (?). Two salts are formed.

Formulate the action (Fig. 17). In doing this, show the

$$
\begin{array}{rcccl}
 & KCl \rightleftarrows & K^{\cdot} & + Cl' & \\
 & AgNO_3 \rightleftarrows & NO_3' & + Ag^{\cdot} & \\
 & & \uparrow\downarrow & \uparrow\downarrow & \\
\text{(dsolvd.)} & & KNO_3 & AgCl & \text{(dsolvd.)} \\
 & & & \uparrow\downarrow & \\
 & & & AgCl & \text{(solid)}
\end{array}
$$

Fig. 17

three main physical components of each of the original solutions and the relations of these components (in equilibrium) to one another in each case. Show also the molecular products

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formed when the solutions are mixed. Assuming that the solutions are approximately normal [R 148], ascertain the proportions in which the original components are present before mixing (Appendix VI). Learn also to what extent the molecular products will be formed by union of the ions (Appendix VI), and, in the case of an insoluble substance, how complete will be the precipitation (Appendix IV). On the basis of this complete information, explain in detail, and one by one, in what way, and to what extent, each of the six original components is affected by the results of mixing.

Name the components of the filtrate and explain how each is affected by the evaporation and crystallization.

How does the formation of the precipitate of silver chloride illustrate **63** *d* (1)? Upon what factor does the completeness of the change depend? Is, or is not, silver chloride a highly ionized substance [R 332]?

Aside from double decompositions, what means have we for learning of what radicals a salt (like silver nitrate) is composed?

b. To a little cupric sulphate solution in a test-tube add sodium hydroxide solution (?). Exactly as in **64** *a* (second par.), formulate, study and explain the whole action. How does this illustrate (1) of **63** *d*?

To what classes of ionogens do the four molecular substances respectively belong?

c. To a little cupric sulphate solution add a little dilute hydrochloric acid (?). In what respects does the result differ from those in *a* and *b*, and why? Can any acids be prepared by precipitation, and if so, which? Give illustrations.

65. Bases and Acids: Hydroxide-ion and Hydrogen-ion: Indicators.

a. Examine distilled water in respect to (a) taste, (b) behavior with litmus, (c) conductivity (done already, **61** *b*).

b. Dissolve a small piece of sodium hydroxide in water and examine the solution in respect to (a) taste, by diluting a little and tasting one drop, (b) behavior with litmus, (c) behavior with phenolphthaleïn, (d) conductivity (see **61** *d*). These properties belong to aqueous solutions of all bases. Aside from the water, what component alone is common to all such solutions and has the above properties?

c. Examine an aqueous solution of hydrochloric acid in respect to (a) taste, (b) behavior toward litmus, (c) behavior with phenolphthaleïn, (d) conductivity (see **61** *e*), (e) action on a piece of marble, (f) action on an iron nail (clean this with the file before use). These properties are shown by all aqueous solutions of acids. Aside from the water, what component

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alone is common to all such solutions and has these properties?

d. Take the solution of hydrogen chloride in toluene (**61** *h*) and examine it in respect to (a) conductivity (see **61** *h*), (b) action on a piece of marble, dried in advance by heating in a dry porcelain dish for a few moments, (c) action on an iron nail (clean as before). Be sure that perfectly dry vessels are used in these experiments. What substance identified in *c* is absent from this solution? What difference between water and toluene, as solvents, does this result indicate? In what three other respects would the two solutions of hydrogen chloride be found to differ?

66. Ionic Chemical Changes: I. Union and Disunion of Ions: Neutralization (Union of $H^{\cdot}$ and OH'). (Two students working together.) A considerable chemical change may occur not only in precipitation (see **64**), but also when ions unite to form a substance which, although soluble, is very little ionized by water. Such changes are illustrated in **66** and **67.**

Weigh out 5 g. (laboratory scales) of potassium hydroxide, dissolve it in 50 c.c. of distilled water, and pour the clear solution into a burette (Fig. 2, p. 7). Measure 10 c.c. of concentrated hydrochloric acid in the graduated cylinder, mix it in a small beaker with 50 c.c. of distilled water, and pour this into a second burette. Now, into a small beaker or flask run 15 c.c. of the acid solution from the second burette, and then add to it two drops of phenolphthaleïn solution. Place the vessel under the first burette, read the level of the liquid in the burette, and allow the alkali to run into the acid drop by drop, stirring constantly, until the last drop confers the faintest perceptible pink tinge on the whole solution. If you do not at first succeed in stopping at the right point, repeat the experiment. Note the volume of alkali used. Concentrate the solution on the sand bath until a drop deposits crystals on cooling, and then remove the dish from the sand bath promptly and set it aside.

When sufficient crystals have appeared, dry them with filter paper and examine with respect to (a) form, (b) taste, (c) exposure to moist air, (d) action of a solution on litmus, (e) conductivity of aqueous solution (done already, **61** *c*). Construct a table comparing the substance in these respects with the materials from which it was made. Compare the substance with potassium chloride on the side-shelf. How should you determine whether a substance obtained in this way contained "water of crystallization" or not? Make the necessary experiments (?). Wash out the burettes.

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Following the directions in **64** *a* (second par.), formulate, study, and explain the whole action. Note, however, that there is here no insoluble substance. Show how this experiment illustrates **63** *d* (2).

Express the change involved in every neutralization of highly ionized substances by means of the simplest equation. How may neutralization be defined, in terms of the hypothesis of ions? How may it be defined, taking account of *all* the facts, but omitting all reference to ions

Calculate the approximate concentration, in terms of a normal solution as unity, of the potassium hydroxide solution used above (?). From the volumes of alkali and acid used in neutralizing, calculate the concentrations of the diluted hydrochloric acid, and of the concentrated acid employed to make it, expressing the concentrations in terms of a normal solution. Calculate the number of grams of hydrogen chloride per liter in the dilute and concentrated acids, respectively.

67. Neutralization of Slightly Ionized and of Insoluble Substances.

a. Consider the degree of ionization of acetic acid (Appendix VI). To neutralize 1 liter of normal acetic acid, would more or less alkali be required than to neutralize 1 liter of normal hydrochloric acid? In what way, precisely, would the details of the change be different in the case of acetic acid [R 356]? Name some of the consequences of this difference [R 357–358].

b. Dilute a few drops of cupric sulphate solution with water and add excess of sodium hydroxide solution (?). Fit a filter paper properly into a funnel (Fig. 3, p. 9). Filter the mixture, and wash the precipitate (?) repeatedly with distilled water to remove soluble substances. Now place a clean test-tube below the funnel, perforate the bottom of the filter paper, and wash the precipitate through into the test-tube by means of a stream of water from the wash-bottle. To the suspended cupric hydroxide, cautiously add dilute hydrochloric acid in amount just sufficient to give a clear liquid. Concentrate the liquid on the sand bath until a drop, removed to a watch-glass, shows signs of crystallizing when cold. Then remove the dish promptly from the sand bath and allow it to cool. Examine the crystals (?).

Formulate this action as in **64** *a*, taking account, however, of the fact that one of the interacting substances is an "insoluble" solid [R 349]. Describe in detail the stages through which the final production of solid cupric chloride is accomplished.

To what class of ionic chemical changes [R 360] does the

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foregoing action belong? Answer the same question in regard to the precipitations of salts in **64**.

68. Ionic Chemical Changes: II. Displacement.

a. Place several pieces of granulated zinc in a dilute solution of cupric sulphate and set aside until the change is complete (test?). Occasional agitation will hasten the change (why?). Filter. What is the precipitate [R 361]? Before examining the filtrate, take a few drops of cupric sulphate solution and a like amount of zinc sulphate solution in two test-tubes. Dilute each solution with water, and add to each ammonium sulphide solution (?). What is the precipitate in each case, and what ions are required to form it?

To the filtrate from the first part of this experiment add ammonium sulphide solution (?). What ions were present in the filtrate? What changes did the zinc and the cupric ions, respectively, undergo in the first part of the experiment? Formulate this change in an equation. In the course of this experiment, what becomes of the molecular cupric sulphate (**63** *d* (3))?

What substances could have been substituted for the cupric sulphate without affecting the result? What substances, beside zinc, would have precipitated copper (Appendix VII)? What other elements, beside copper, are displaced by zinc?

Which of the elements displaced by zinc did we prepare in quantity by an action like the present (**18**). Formulate this action in terms of the hypothesis of ions. What were the products of the action of zinc upon concentrated sulphuric acid (**16** *d*)? What is the chief component of this form of the acid (Appendix VI)? If this component interacted with the zinc, to what class of chemical changes did this action belong?

b. Formulate the actions in **16** *a* in terms of the hypothesis of ions. Explain in terms of the hypothesis the differences in activity of the various metals [R 362].

c. Examine your notes on Chap. VIII. Formulate the following actions in terms of the hypothesis of ions:

Free chlorine and bromide-ion (**43** *b* and **45** *g*).
Free chlorine and iodide-ion (**47** *c* and **50** *a*).
Free bromine and iodide-ion (**47** *d*)
Free iodine and sulphide-ion (**49**).

Arrange these four elements in a series similar to the electromotive series of the metals (Appendix VII). Where should you place fluorine in this series [R 241]? Can you indicate the approximate position of oxygen [R 239, 241]?

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69. Ionic Chemical Changes: III, IV, V. In addition to union or disunion of ions (I), and displacement (II), there are three other ways in which ions may undergo chemical change.

One of these (III) was illustrated in **29** *a* and *b*, in **54** *b*, in **57** *a* and *b*, in **59** *a*, *b*, and *c*, and in **60** *c* (?).

Another (IV) was illustrated in **29** *a* (?).

Still another (V) was illustrated in **61** (?).

Define each of these three classes of ionic chemical change and formulate the illustrations anew so as to show how the actions cited belong to the class illustrated.

Re-examine the seven ways in which ionic substances are removed, and dissociation of the parent molecules is promoted (**63** *d*), and indicate that one of the five classes of ionic change to which each of the seven belongs.

70. Non-Ionic Actions. In previous class-room and laboratory experiments we have observed the formation of ionogens in other ways than those illustrated in this chapter. These ways are non-ionic, or not distinctly ionic. Give illustrations of such of these ways as you recall: acids, two ways; bases, one way; salts, four ways, together with the reference numbers of the laboratory experiments in which they occur.

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CHAPTER XI.

SULPHUR.

71. Sulphur.

a. In a dry test-tube place a very small piece of roll sulphur with 2–3 c.c. of carbon disulphide, and shake (?). Allow the clear solution to evaporate spontaneously (i.e., without the aid of heat) in a watch-glass [Hood], and describe the crystals [R 138] (?). See Note 25, p. 10.

b. In a dry test-tube place about 5 g. of roll sulphur, melt the substance with the least possible application of heat (the material must remain pale-yellow), and pour the melt into a beaker of cold water. Dry some of the product with filter paper and test its solubility in carbon disulphide as in *a.*

c. Melt about 10 g. of sulphur in the same test-tube, and heat the body until it boils (?). Note the changes in color and fluidity that occur. To learn the nature of the substance formed by heating, chill the sulphur while it is boiling vigorously by pouring it suddenly into cold water (?). Note the physical state of the product, dry a part with filter paper, and examine its solubility in carbon disulphide (?). Set the remainder aside for a few days, and then study its appearance and solubility again (?). Keep also the test-tube from which it was poured, and examine, at the same time, in both these respects, the sulphur which remained adhering to its walls and was not cooled so suddenly (?). Account for the change when sulphur is heated, and the differing results of rapid and slow cooling [R 369].

Why are we convinced that none of the changes was due to interaction with the water?

d. Mix in a mortar 2 g. of iron filings and 1 g. of powdered sulphur. Transfer to a dry test-tube and heat gently (?). When cool, break the test-tube in a mortar and use the black product (?) in **72** *a.*

Recall and record here a case of the union of sulphur with a metal which was observed previously.

72. Hydrogen Sulphide [Hood].

a. Place a part of the product from **71** *d,* or about 1 g. of ferrous sulphide, in a test-tube and add a little dilute hydrochloric acid (?). Note the odor of the gas, and apply to it a strip of filter paper dipped in lead nitrate solution [R 705] (?).

b. With a Kipp's apparatus generating hydrogen sulphide,

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or with the laboratory supply of the gas, connect a glass nozzle. When the air has been displaced, set fire to the gas. Describe the color of the flame. Hold a porcelain dish in the middle of the flame for a few moments (?). What substance is deposited, and must, therefore, exist uncombined in the interior of the flame? What other substance does this justify us in assuming to be liberated in the same region? What do these facts indicate regarding the stability of the gas when heated, and the difficulty, therefore, of making the compound by the direct union of its elements? What are the products of the complete combustion of the gas, and in what two stages does this combustion take place? Make equations showing both stages.

73. Properties of Aqueous Hydrogen Sulphide: I [Hood].

a. Take about 15 c.c. of water in a carefully cleaned test-tube and saturate (test? Note 36, below) it with hydrogen sulphide. Test the solution with litmus paper [R 347] (?). Pour one-third or less of the solution into another test-tube and boil this portion vigorously, noting from time to time the odor of the vapor. Can this gas be driven off completely by boiling? Does hydrogen chloride solution behave in the same way or differently [R 182]?

b. Divide the remainder of the solution into two parts and add 2–3 g. of iron dust (pulverized iron) to one of them. Shake vigorously and then allow the mixture to stand (?). After a few minutes collect the insoluble matter upon a filter and wash until it no longer smells of hydrogen sulphide. Transfer the precipitate to a test-tube by puncturing the paper and washing through. Add dilute hydrochloric acid to the product and note the odor (?). What substance must have been present in the precipitate, and how was it formed? Account for the extreme slowness of the action of iron upon the solution of hydrogen sulphide [R 374].

c. Allow the third portion of the solution made in *a* to stand for some days exposed to the air (?). Explain the turbidity.

d. If **49** was performed, record here the action which took place. If **49** was not performed, place a single crystal of iodine in 5 c.c. of water and saturate (test? Note 36, below) the liquid with hydrogen sulphide [R 238] (?).

What ionic substance is shown by the first part of **73** *a* and by **73** *b* to be present in the solution of hydrogen sulphide [R 374]? Explain the actions in *c* and *d* in accordance with the hypothesis of ions.

e. To 2–3 c.c. of potassium dichromate solution add dilute sulphuric acid in large excess (?). What change may be

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assumed to have taken place? Now saturate (test? Note 36, below) the mixture with hydrogen sulphide (?). What are the colors of the solution and of the precipitate, respectively? Show that two kinds of ionic chemical change are here illustrated.

f. Take 2–3 c.c. of potassium permanganate solution and treat exactly as in *e* (?). Answer the same questions (?). What chemical property of hydrogen sulphide is illustrated in *e* and *f*?

Note 36. — To learn whether a liquid is saturated with a gas, withdraw the delivery tube while the gas is issuing, cover the mouth of the vessel quickly with the thumb or the palm of the hand in such a way that the gas above the liquid has no time to escape (why?), and shake vigorously. If the thumb now adheres to the mouth of the vessel, the liquid is not yet saturated (why?). If the liquid is saturated, what will be the pressure of the gas over it after shaking [R 153]? If air is allowed to displace the gas over the saturated liquid, what effect will be observed on shaking as described above?

74. Properties of Aqueous Hydrogen Sulphide: II. Sulphides [Hood].

a. What was the reaction of aqueous hydrogen sulphide towards litmus (**73** *a*)? What ionic substances are present?

b. Take about 6 c.c. of sodium hydroxide solution and saturate (test? Note 36) it with hydrogen sulphide (?). Test with litmus (?) and use in *c*, *d*, *e*, and *f*. How should you proceed to prepare normal sodium sulphide (solid)?

c. To a few drops of the solution prepared in *b* add dilute hydrochloric acid (?) (see **75** *b*).

d. To a few drops add some bromine-water (?).

e. To a larger portion of the same solution add a little powdered roll sulphur and shake from time to time. Is sulphur soluble in water? What is here to be inferred [Note 35, p. 48]? When the solution has become very yellow (?) in color, filter. Acidify the filtrate with dilute hydrochloric acid (i.e., add more than an equivalent amount of the acid) (?). Recall an experiment with iodine which resembles this experiment with sulphur (?).

f. Allow the remainder of the solution from *b* to remain exposed to the air for several days (?). When a change in color has occurred, add dilute hydrochloric acid in excess (?). Explain.

g. Take five clean test-tubes and obtain 2–3 c.c. of the solution of each of the following substances. Dilute each specimen with 10–20 c.c. of water and saturate (test?) with hydrogen

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sulphide: (a) Cupric sulphate (?), (b) Lead nitrate (?), (c) Cadmium sulphate (?), (d) Zinc acetate (?), (e) Ferrous sulphate (make a solution of ferrous-ammonium sulphate [R 754] and use it for this [Note 37, below]).

Explain the precipitation in accordance with the hypothesis of ions.

Pour away a part of the contents of each test-tube, add a large excess of dilute hydrochloric acid, and shake (?). Explain the results. Divide the metallic sulphides obtained in this experiment into two classes, and characterize those classes.

What property of hydrogen sulphide has been illustrated in *a*, *b*, and *g*?

Note 37. — Ferrous-ammonium sulphate [R 754] is preferred to ferrous sulphate because it becomes less rapidly impure through oxidation by the air. In making equations, disregard the ammonium sulphate.

75. Ionic Chemical Changes: Formation of an Inactive Acid.

a. To 2–3 c.c. of sodium acetate solution add an equivalent amount of dilute sulphuric acid, and warm gently. One product may be recognized by its odor (?).

Formulate, study and explain this action according to the directions in **64** *a* (second par.). Write a simple equation expressing the chief change which occurs.

b. Consider the action between sodium-hydrogen sulphide and hydrochloric acid in **74** *c*. Formulate, study and explain this action as in **64** *a* (second par.), modifying the scheme of formulation to suit the case. Does the escape of the hydrogen sulphide assist materially in making the action more nearly complete? Does it assist at all? What property does the escape of the hydrogen sulphide as a gas show this substance to possess?

c. Make a single general statement describing all the cases in which, when ionogens are mixed, and no precipitation or volatilization occurs, a fairly complete chemical change will nevertheless take place (see **66**).

Give a list of acids (Appendix VI) which might be formed in accordance with the principle embodied in your statement.

Could any bases be formed in accordance with the same principle? Illustrate (Appendix VI). Could any salts be so formed (Appendix VI)?

76. Hydrolysis.

a. Dissolve a single crystal of sodium sulphide in water, and test the solution with litmus paper (?). What ionic substance

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causes this reaction? Which of the two substances taken is capable of furnishing this ion? Formulate the interaction of the two original substances and explain it [R 375].

b. Test with litmus paper the solution of sodium carbonate (?). Explain (Appendix VI). Of what sorts of radicals must a normal salt be composed in order that the solution may show an alkaline reaction [R 344]?

c. Test with litmus paper the solutions of cupric sulphate (?) and ferric chloride (?), and account for the result [R 344]. Of what sorts of radicals must a normal salt be composed in order that the solution may show an acid reaction? Why is sodium chloride solution neutral? Define hydrolysis.

77. Sulphur Dioxide.

a. Touch with a warm platinum wire a bit of sulphur, and bring the wire with the adhering sulphur again into the flame. Withdraw, and note the color of the flame of the burning sulphur and also the odor (?).

b. Heat in a hard glass test-tube a few particles of iron pyrites. What is the sublimate? What gas is evolved?

c. [Hood] If sulphur dioxide gas is not furnished in the laboratory from cylinders of the liquid,* it may be prepared for use in **78** or **83** as follows: Fit up a flask (250 c.c.) as in Fig. 8 (p. 20), and attach to it by rubber connections a gas washing-bottle (Fig. 18). This bottle is to serve here as a safety vessel (why and how?) and is to be left empty. If **78** is to be performed, a second, similar gas washing-bottle will be required to dry the gas, and will contain enough concentrated sulphuric acid to immerse the longer tube to a depth of half an inch. Attach the empty bottle with the shorter tube next to the generating flask (why not the reverse?). Place about 10 g. of copper nails in the flask. Test the apparatus to see that it is air-tight. Add 10–15 c.c. of concentrated sulphuric acid.

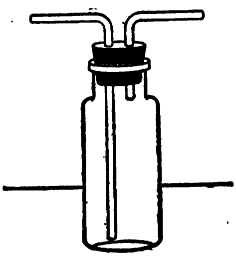

Fig. 18

Heat the flask and contents by means of a sand bath. Leave the cork out at first and suspend in the acid a thermometer. Note the temperatures at which chemical action becomes perceptible (?) and at which it is conspicuous (?). Why cannot

* If the gas is not so furnished, **77** and **78** should be taken up after **82**.

dilute sulphuric acid be used? Connect the apparatus and continue heating to obtain the gas needed in **78** and **83**.

d. Allow the generating flask with its contents to remain over night, and then examine and describe all the contents (?).

78. Molecular Weight of Sulphur Dioxide [Quant. Hood]. Clean and dry a 250 c.c. flask and provide it with a tightly fitting cork. Weigh the flask and cork. This gives the weight of the flask filled with air. Now fill it completely with sulphur dioxide, by downward displacement of air, cork, and weigh again. To insure its being full, repeat this operation till no increase in weight occurs. Finally, allow the gas to escape, and determine its volume by filling the flask with water up to the cork and weighing again. Observe the temperature and pressure of the atmosphere.

To obtain the weight of the empty flask and its cork, subtract from the weight of the vessel filled with air the weight, under the observed conditions, of a volume of air equal to its content (1 liter of pure, dry air weighs 1.293 g. under normal conditions, or the G.M.V. holds 28.955 g. of air).

The difference between this corrected weight and that of the flask filled with sulphur dioxide is the weight of the latter. Reduce the volume of the gas to normal conditions and calculate the weight of the G.M.V. (22.4 l.) and of 1 l.

Enumerate carefully all the sources of error to which you should expect this way of determining the density of a gas to be liable. In doing this, consider each detail of the operation very critically.

79. Preparation of Sulphuric Acid (Two students working together). Obtain a distilling-flask (25 c.c.), rubber connections for a safety bottle, a screw-clamp, and a Chapman pump from the storeroom. Fit up with your one-liter bottle the apparatus as in Fig. 19. Charge the hard glass tube with about 10 g. of granular pyrite,* and place a small, loose plug of asbestos just beyond the pyrite to retain any unburnt sulphur. Put into the distilling-flask about 10 c.c. of pure concentrated nitric acid [Side-shelf]. The safety bottle, half filled with water to show the rate at which air is being drawn through the apparatus, is attached to the water pump. The total air admitted is regulated by the screw-clamp between the pump and the safety bottle, while the proportions which pass over the pyrite and

* In case very pure pyrite is not available, it is better to depart from the common manufacturing process by substituting a boat containing a little sulphur.

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which carry over the nitric acid vapor, respectively, are regulated by pinching one of the tubes with the finger and thumb.

First heat the pyrite in a very slow stream of air until the sulphur burns. Then warm the nitric acid, and, by pinching the tube admitting air to the pyrite-burner, divert part of the air current so that it may carry over a little of the vapor of the acid. Heat the pyrite strongly and continuously. Repeat the introduction of air laden with nitric acid at intervals, when-

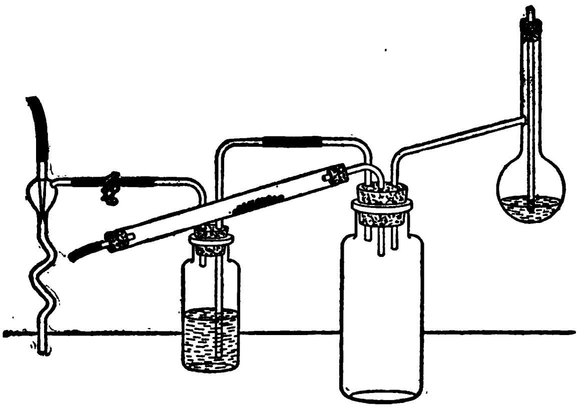

Fig. 19

ever the disappearance of the red fumes in the bottle shows that a further supply is needed.

After a crust of white crystals (?) has formed in the bottle (there may be considerable delay before crystallization starts), remove the attachments and blow the gases from the interior by means of the air blast. If crystallization fails to begin after a reasonable time (note that an interaction even between the molecules of gases may be slow, in spite of the completeness of the mixing), the cause is either the introduction of too much water along with the nitric acid, or the high temperature produced by the chemical actions taking place in the bottle. Removing the attachments and cooling the bottle in a stream of water frequently brings crystallization about.

Add 4–5 c.c. of water and wash down the crystals with it. Describe all that happens. If more of the product is required, the apparatus may be connected up again and a further supply of sulphur dioxide drawn into the bottle, and subsequently

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more nitric acid vapor can be added. Finally any remaining crystals may be decomposed by water.

Filter the liquid in the bottle through a very small filter paper into a dish, rinsing the bottle with 2–3 c.c. of water, and evaporate on the sand bath [Hood] until the liquid begins to fume strongly (?). This will remove any nitric or nitrous acid that it may contain. Use the result for **80** *a* and *b*.

80. Properties of Sulphuric Acid.

a. Dip a match-stick into the liquid from **79**, and make marks on a sheet of paper. Set both paper and stick on a radiator (?). What property of the acid is here observed?

b. After the acid prepared in **79** is cold, dilute it with 2–3 volumes of water. Test the solution with litmus paper (?). Add to it barium chloride solution (?). To learn whether the action is easily reversible, add pure hydrochloric acid to the mixture (?). The formation of this precipitate, and its insolubility, furnish a distinctive test for what radical? Which substances contain this radical? What property of sulphuric acid is shown in *b*?

c. Pass a current of hydrogen sulphide through 2–3 c.c. of concentrated sulphuric acid. Note the odor (?) and precipitate (?). What property of sulphuric acid is shown in *c*? What other evidence of this property have we previously observed (see **16** *d* and **52**)?

d. Place a small piece of sulphur in 2–3 c.c. of concentrated sulphuric acid, and heat (?). Note the odor (?).

e. Heat a little charcoal with sulphuric acid and note the odor (?). What property of sulphuric acid is shown in *d* and *e*? Why would not dilute sulphuric acid show this property?

f. [Hood] Take 2–3 c.c. of concentrated sulphuric acid in a test-tube. Suspend a thermometer so that the bulb is completely immersed in the acid. Heat the contents of the tube by means of a small flame and note the temperature at which any effect (?) is observed, and that at which it is conspicuous. Relate this temperature to that observed in **77** *c*. [CAUTION! During the heating remember that, if the tube should crack, the hot acid may splash on the clothes and hands and produce severe burns. Exercise proper caution. Be careful not to wash out this tube until the acid has cooled.]

81. Sulphuric Acid as a Dibasic Acid.

a. (Two students working together). Fill a burette with a solution of potassium hydroxide made as in **66**. Add 15 c.c. of concentrated sulphuric acid slowly to 35 c.c. of water in a beaker, and fill another burette with the diluted acid, when cold. Ascertain as in **66** what volume of the alkali will neutralize 5 c.c.

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of the acid. Concentrate the mixture by evaporating to about 10 c.c., remove the dish from the water bath, and allow the resulting solution to crystallize. Dry the crystals on filter paper. To a second portion of the acid (use no phenolphthalein. Why?), twice as great as before, add exactly the same amount of the alkali. Evaporate to about 5 c.c. and treat as before.

Compare the two lots of crystals as regards (a) form, (b) taste, (c) reaction of their solution towards litmus. Confirm by studying the same properties of the purer substances found on the side-shelf. Explain the differences between your own preparations and those on the side-shelf, if any are observed. Explain, in terms of the hypothesis of ions, the difference in the reactions of the two products towards litmus.

Formulate, study, and explain the actions, as in **64** *a* (second par.). Take the components of the original solutions [R 346] one by one, and describe what happens to each, (a) during complete neutralization, (b) during semi-neutralization in the second part of the experiment.

What would be the effect of heating perfectly dry specimens of each of the salts [R 390]?

How many grams of potassium-hydrogen sulphate are required to give 1 liter of a solution of normal concentration in respect to (a) potassium-ion, (b) hydrogen-ion, (c) sulphate-ion?

b. Make a solution of sodium bicarbonate and test it with litmus paper (?) and with Congo red paper (?). Why do some acid salts show little or no acid reaction towards indicators?

Define carefully, and illustrate, the terms: normal (neutral) salt, acid salt, and basic salt [R 359].

82. Sulphates. Place some ferric sulphate in a porcelain crucible supported on the clay triangle, and heat strongly [Hood] with the blast-lamp, continuing the heating after all the water has been driven off (?). What are the properties of the vapor given off (?), and what is it? What is the residue? Relate this result to that in **80** *f*. Recall action of heat on dehydrated gypsum (**23** *f*). Classify the sulphates in accordance with this distinction.

83. Properties of Sulphurous Acid [Hood]. Use a stream of sulphur dioxide from a cylinder of the liquefied gas, or from the apparatus described in **77** *c*.

a. Pass a stream of sulphur dioxide for a few minutes into a test-tube full of water. Test the solution with litmus paper (?). What compound is present in the aqueous solution of the gas? Note also the odor of the liquid (?). Formulate the interac-

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tion, showing all the substances present. Divide the solution into four portions.

b. Boil one portion persistently [Hood], noting from time to time the odor and reaction towards litmus (?). In respect to the result, does the solution of this gas resemble that of hydrogen sulphide, or that of hydrogen chloride?

c. To another portion add barium chloride solution (?). To ascertain whether this action is easily reversible, add excess of pure hydrochloric acid (?).

d. To the third portion add bromine-water (?) until the color is permanent (?). Now add barium chloride to the mixture (?) and then pure hydrochloric acid (?).

What chemical properties of sulphurous acid are illustrated in *a, b, c,* and *d,* respectively?

e. Leave the fourth portion of the sulphurous acid for several days exposed to the air in an open test-tube or bottle. Then add barium chloride and pure hydrochloric acid, and compare the result with that in *c.*

f. To 2–3 c.c. of potassium dichromate solution, add three or four equivalents (a large excess) of dilute sulphuric acid. What substances does the mixture contain? Lead a stream of sulphur dioxide through the solution until no further change is observed (?).

g. Take 2–3 c.c. of potassium permanganate solution, treat as in *f* (?), and answer the same questions (?).

h. Fill a bottle with the gas by downward displacement, introduce some moistened litmus paper or grass, and close with a glass plate (?).

What properties of sulphurous acid are illustrated in *e, f, g,* and *h,* respectively?

84. Sulphites.

a. To 1 g. of sodium sulphite add any dilute mineral acid (that is to say, one of the common acids, but not an organic acid such as acetic) (?). Formulate this action completely.

b. Dissolve a minute amount of sodium sulphite in water and add bromine-water in excess (test? The color must remain). Remove the excess of bromine by boiling. Add barium chloride solution (?) and then pure hydrochloric acid (?). Compare this experiment with that in **83** *d,* consider whether it is probably the molecular sodium sulphite, or the sulphite-ion, which is oxidized, and make the equation accordingly.

c. Heat persistently about 1 g. of sodium sulphite in a porcelain crucible, supported on the clay triangle over a blast-lamp. When cool, acidify with hydrochloric acid (?) and note the odor. If any sulphur is precipitated, account for its formation.

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d. Place about 1 g. of sodium bisulphite in a hard glass test-tube and heat cautiously with the tube in a horizontal position (why?). Note the odor (?) and whether any vapor condenses (?). This behavior is typical of that of many acid salts. Why is the behavior of potassium bisulphate somewhat different (81 *a*)? What would be the final effect of heating sodium bisulphite more strongly and for a longer time?

85. Thiosulphates.

a. Dissolve about 5 g. of sodium sulphite in about 20 c.c. of water in a small flask. Add 4–5 g. of flowers of sulphur to the solution and boil gently over a small flame for 10–15 minutes. Filter off the clear yellow solution and divide into two parts.

b. To one portion add excess of any dilute mineral acid (?). Note the odor.

c. Take 10 c.c. of potassium iodide solution and dissolve in it a few small crystals of iodine [R 235] (?). Now pour the second portion of the solution from *a* slowly into this mixture [R 396] (?). How can this action be used for estimating the quantity of free iodine, and what substance then acts as the indicator? For what purpose was the potassium iodide employed?

d. Heat persistently about 1 g. of sodium thiosulphate in a porcelain crucible over a blast-lamp (?). Note the appearance of the residue. When cold, add dilute hydrochloric acid (?) and identify the products. If any odor was observed during the heating, can you now account for it?

86. Reduction of Sulphur Compounds. Mix a pinch of any salt of a sulphur acid with an equal amount of anhydrous sodium carbonate. Slightly char the end of a match from which the head has been removed, and rub the charred part, which should be about an inch in length, with a heated crystal of hydrated sodium carbonate. Moisten the above mixture with water, place some of it on the end of the match, and heat in the reducing region of a small Bunsen flame. Put the result on a clean silver coin lying in a watch-glass and moisten with one drop of water (?). Then add some dilute mineral acid and note the odor (?). This, known as the "hepar" test, is a test for sulphur in any form of combination.

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CHAPTER XII.

THE ATMOSPHERE, NITROGEN, AMMONIA.

87. Preparation of Nitrogen from Air. Place a large plug of copper turnings in the center of a hard glass tube. Fit with corks and short glass tubes, and connect with the short tube of the aspirator (Fig. 7, p. 16). Fill completely with water the bottle and long tube of the aspirator and close the latter with a screw clamp [Storeroom]. Arrange a vessel to catch the water discharged. Now heat the copper red-hot and then partly open the clamp so as to allow the water to be syphoned off in a slow stream. The air will pass over the heated copper. What change does the copper undergo, and what collects in the bottle? After three-fourths of the water has run out, close the clamp, disconnect the hard glass tube, attach a delivery tube in its place, elevate the end of the syphon, and replace the nozzle by a small funnel supported by a clamp. Pour water into the funnel, and drive the gas over into a bottle of water inverted in the pneumatic trough. Ascertain whether this gas supports combustion. Describe the gas as regards color and smell. What other gaseous substances, besides nitrogen, does this gas contain?

Other ways of removing oxygen from the air are described elsewhere (**14**, **88**, and **94** *d*).

88. Proportion (by Volume) of Oxygen in the Air [Quant.] (from Cooley's *Laboratory Studies*). Provide a large test-tube with a two-hole rubber stopper. Into one hole fit a short piece of glass tubing terminating in a rounded nozzle, the tip of which projects but little beyond the bottom of the stopper. Into the other hole fit a short glass rod. Test the apparatus for air-tightness. Connect the upper end of the glass tube with a short-stemmed funnel by means of a piece of rubber tubing (15 cm. long) as in Fig. 20, and support the funnel in a clamp.

Disconnect the test-tube, temporarily, and remove the glass rod from the stopper. Prepare an alkaline solution of potassium pyrogallate by mixing 3 c.c. of pyrogallic acid solution with 20 c.c. of a solution of potassium hydroxide specially prepared for this experiment [Side-shelf], and pour this into the funnel. Now open the clamp and permit this solution to fill the rubber and glass tubes completely down to the opening of the nozzle. Replace the test-tube, fitting the stopper tightly

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into its mouth. Finally, reinsert the glass rod, and so inclose a volume of air equal to the content of the test-tube and at the temperature and pressure of the atmosphere. These operations should consume as little time as possible, as the alkaline solution gradually absorbs oxygen from the air of the room, and thereby becomes useless for further absorption.

Now open the clamp, taking care not to warm the test-tube by handling. A few drops of the alkaline solution will enter

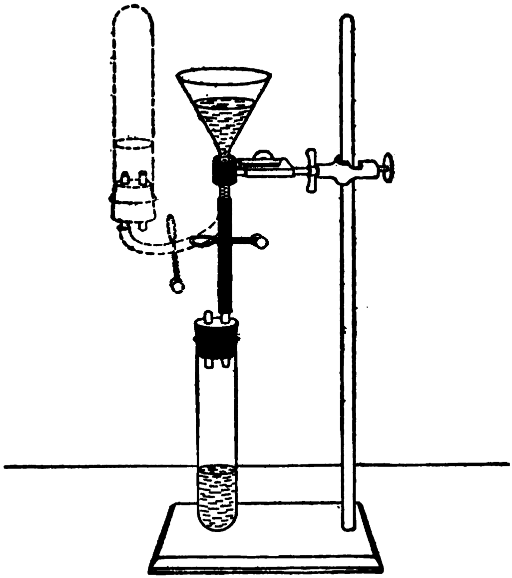

Fig. 20

the test-tube, and, as the oxygen is absorbed, more of the solution will flow in. Close the clamp and invert the test-tube once or twice in order to bring the liquid thoroughly in contact with the inclosed air. Finally, while the test-tube is in the inverted position, reopen the clamp and equalize the levels of the liquid in test-tube and funnel by raising or lowering the former. Then close the clamp, restore the test-tube to its original position, and mark the positions of the surface of the liquid and of the bottom of the stopper by means of paper labels or rings cut from rubber tubing.

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Disconnect the test-tube and wash out the liquid, taking care not to get the alkaline solution upon the hands. Then, by means of a burette filled with water, measure the volumes required to fill the test-tube up to the lower and upper marks respectively. The former is the volume of the oxygen, the latter that of the air. Calculate the percentage of oxygen in the air by volume.

89. Other Components and Density of Air.

a. Place 2–3 c.c. of clear barium hydroxide solution in the bottom of a small beaker and leave it exposed to the air for some hours (?).

b. Blow air from the lungs through a glass tube into 2–4 c.c. of clear barium hydroxide solution (?). Explain.

c. How may the presence of aqueous vapor in air be demonstrated (**27** *a*)? How may its quantity be measured?

d. The weight of a measured volume of air, or of nitrogen, may be determined by the method described in **112**. From the data so obtained the density may be calculated.

90. Nitrogen.

a. Place about 10 g. of pure sodium nitrite and about 8 g. of ammonium chloride in a 250 c.c. flask fitted with safety and delivery tubes (Fig. 8, p. 20). If *b* is to be performed, insert between the flask and the delivery tube a U-tube containing calcium chloride for drying the gas.

Clamp the flask by the neck to a ring-stand, add about 15 c.c. of water, and warm gently [CAUTION!]. As soon as the action begins remove the flame, bring a dish of cold water under the flask, and cool it for a few seconds at a time so that the action may not become too violent, but may run uniformly. After sufficient time has been allowed for the displacement of air from the apparatus, fill a bottle with the gas over water in a pneumatic trough. Has the gas odor or color? Does it support combustion?

b. (Two students working together). In a piece of hard glass tubing, fitted with corks and short pieces of glass tubing, place a porcelain boat half filled with powdered magnesium. Connect one end of this tube to the outlet tube of the flask in *a* generating nitrogen. Heat the magnesium strongly (two Bunsen burners may be necessary). What action is noticed? What is the color of the product? Transfer the contents, when cold, to a dry test-tube, close with a cork, and use in **91** *b*. May the same product be formed when magnesium is heated in the air? What other compound would be formed under the latter conditions?

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91. Ammonia.

a. Fit a small flask with a cork and L-shaped exit tube, and connect the latter with a U-tube. Put a little water in the bend of the latter so as just to close the passage. Test the apparatus for air-tightness. Place in the flask a mixture of powdered quicklime and ammonium chloride, about 10 g. of each, and warm gently [Hood]. After the air has been displaced, the whole of the gas should dissolve in the water. Use this solution of ammonium hydroxide in **92**.

If required to determine the density of ammonia, which of the various methods should you select (**15** *a*, **78**, or **112**)?

b. To the product from **90** *b* add a little water, boil, and note the odor (?). What other substances would behave in the same way as magnesium nitride?

c. Heat a small piece of gelatine in a dry test-tube and note the odor (?).

92. Ammonium Hydroxide: An Inactive Base: Salts of Ammonium.

a. Test the reaction towards litmus paper of the solution made in **91** *a* (?). What substance is present? Hold a glass rod dipped in concentrated hydrochloric acid over the solution (?). What substance is shown by this test to be present? Formulate the relations (in equilibrium) of all the substances in the solution.

b. Expose 1–2 c.c. of the solution from **91** *a* in an evaporating-dish for 24 hours and then note the odor (?) and test with litmus (?). Heat [Hood] another small portion in an evaporating-dish for some minutes, and note the odor from time to time (?). Does the aqueous solution of this gas behave like that of hydrochloric acid, or like that of hydrogen sulphide? What other gases resemble ammonia in this respect?

c. Neutralize (test ?) the remainder of the solution from **91** *a* with dilute sulphuric acid and evaporate to dryness on a water bath (?). Formulate this action after the model in **64** *a* (second par.), and explain what happens during neutralization to each of the substances present in the ammonium hydroxide solution.

Scrape the residue into the middle of the dish, invert over it a small funnel, the stem of which has been closed with a paper plug, and heat the dish strongly and persistently (?). To learn whether the sublimate is identical with the residue, examine it for the ammonium radical (**92** *d*, below), and the sulphate (**80** *b*) radical.

d. Dilute 1–2 c.c. of ammonium chloride solution and add to it 1–2 c.c. of sodium hydroxide solution (?). Note the odor (?).

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Formulate, study, and explain this action according to the directions in **64** *a* (second par.). Include in the formulation the liberation of the ammonia. What is an inactive base?

The evolution of ammonia when an active base is added to a solution of any ammonium salt is used as a test for the latter. Why would not simply heating the salt by itself (as in **92** *c* and *e*) serve as a test? What salt of ammonium that we have used gives, when heated, no ammonia?

e. Place some ammonium chloride in the middle of an open, hard glass tube. Support this in a very slightly inclined (5°) position by means of a clamp attached close to one end. Put pieces of moistened litmus paper (both colors) in each end, and heat the salt strongly (?). Watch closely the effect on the papers at each end (?). What does this experiment show to be the action of heat on ammonium chloride? Which gas appeared first at the ends of the tube, and why first at both lower and higher ends? What should be the relative speeds, by calculation, of the two gases [R 108]? Why does the second gas reach the ends so very much later than one might expect? Has gravity any influence on the result?

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CHAPTER XIII.

OXIDES AND OXYGEN ACIDS OF NITROGEN.

93. Preparation of Nitric Acid [Hood]. Pulverize about 10 g. of sodium nitrate and place it in a dry retort or distilling-flask [Storeroom]. Cover the salt with concentrated sulphuric acid and wait until this liquid has permeated and moistened the entire mass. Support the vessel by a clamp upon a sand bath and allow the neck of the retort (or side-tube of the flask) to extend to the bottom of a small flask (the receiver). In order that the vapor of the nitric acid may condense, this flask is immersed in a vessel of cold water, and is covered with filter paper which is continually moistened. Heat the retort gently until a sufficient amount of nitric acid has been obtained, and preserve the product in a corked test-tube for use in **97** *a* [CAUTION! Serious wounds may be caused by allowing this liquid to come in contact with the skin]. What is the composition of "concentrated" nitric acid [R 440], and how does the acid here made differ from the "concentrated" acid? What law teaches us to expect that the former will be more active (and dangerous to handle) than the latter?

94. Nitric Oxide.

a. Into a small flask, fitted as in Fig. 8 (p. 20) and containing about 10 g. of copper nails, pour 10–15 c.c. of water and then an equal amount of concentrated nitric acid [Desk]. Collect the gas evolved over water in the pneumatic trough. Note the color of the gases first formed, and observe the color of the pure gas finally collected over the water. Fill two bottles (for *b*, *c*) and the large test-tube (for *d*) with the gas.

The production of colored gases, when copper is added, is used as a test for nitric acid.

b. Into one bottle introduce a burning match (?). Note also the effect of opening this bottle to the air (?). This effect may be used as a test for nitric oxide, or, conversely, for oxygen. How should you apply it for each of these purposes?

c. Into the second bottle lower a deflagrating spoon with a very little burning, red phosphorus (?). What change in volume does the gas undergo in this action?

d. Transfer without loss the nitric oxide in the test-tube to a small beaker filled with water and inverted in the pneumatic

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trough. Fill the test-tube with oxygen and add this to the nitric oxide (?), thus securing equal volumes of the gases. Shake the beaker, keeping the mouth well immersed, until no further change occurs. Transfer the remaining gas, which must be either nitric oxide or oxygen, back to the test-tube. Note its volume, and determine what gas it is (?). What relative volumes are (a) used for the interaction and (b) required by the equation?

How might the proportion of oxygen in the air be determined by application of this interaction?

e. Prepare 10 c.c. of a concentrated solution of ferrous-ammonium sulphate [Note 37, p. 68] (or ferrous sulphate) and divide into three portions. Into one pass a gentle stream of nitric oxide (?). Boil the liquid (?).

f. Add to the second portion of ferrous-ammonium sulphate solution an equivalent amount of dilute sulphuric acid, heat to boiling, and add nitric acid [Desk] drop by drop (mix after each drop) until there is no further action (?). What gas is liberated?

g. Dissolve a single crystal of sodium nitrate in 1–2 c.c. of water, and add a part of this solution to the remainder of the ferrous-ammonium sulphate solution from *e.* Pour concentrated sulphuric acid cautiously and steadily down the side of the test-tube until it forms a considerable layer at the bottom of the tube. Note the brown ring between the layers, and explain by reference to *e* and *f.* This constitutes a delicate test for nitric acid or a nitrate. In what way does the avoidance of mixing (and consequent ring-formation) contribute to the delicateness of the test?

h. Take 2–3 c.c. of concentrated nitric acid in a test-tube, warm it slightly, and lead through it a stream of nitric oxide (?). By waiting until the air has been wholly displaced, make certain whether the colored gas is formed by an interaction of the nitric oxide with the nitric acid, or simply by contact with the air in the test-tube (?).

95. Nitrogen Tetroxide. Fit a hard glass test-tube with a cork and L-shaped exit tube, and see that it is air-tight. Place 8–10 g. of lead nitrate in the tube and clamp it in a horizontal position. Prepare a strong solution of sodium hydroxide by dissolving 2 g. of the solid in 7 c.c. of water and allow the delivery tube to reach the bottom of this solution. Now heat the lead nitrate (?) persistently until gas is no longer given off, or until the liquid is no longer soapy to the touch. If all the gas is not absorbed in the alkali, test the escaping bubbles for oxygen (?). Use the solution in **100** *d.*

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What is the residue? What other nitrate have we decomposed in the same way (**35**)? This behavior when heated is typical of the nitrates of the heavy metals, and may be used for identifying them. Which nitrates, when heated, would leave the metal, instead of the oxide [R 362]? Why do commercial specimens of mercuric oxide [R 657], when heated in the preparation of oxygen, frequently give off a brown gas?

96. Principles Involved in Making Nitric Acid.

a. Addition of copper (**94** *a*) to a liquid containing nitric acid gives red vapors. Is this a test for any substance containing the nitrate radical, or only for nitric acid? Dissolve a little sodium nitrate in water, add a copper nail, and warm (?).

b. Was nitric acid formed in **93** on mixing sodium nitrate and sulphuric acid, before the distillation began? Solve this question by mixing sodium nitrate (finely pulverized) with concentrated sulphuric acid, adding a very little water [Caution] and agitating for a minute or so. Lower a glass rod dipped in ammonium hydroxide solution into the test-tube (?). Apply also the copper test as in *a* (?).

c. Is the action of sulphuric acid upon sodium nitrate reversible? Take 2–3 c.c. of concentrated sodium-hydrogen sulphate solution and add to it an equal or even greater volume of pure [Side-shelf] concentrated nitric acid. Cool the mixture in a stream of cold water and stir with a glass rod (?). The salt solution must be sufficiently concentrated, otherwise the experiment will fail. Examine with a lens the crystalline product that separates out (?). If the action is reversible, what enabled us to obtain a large yield of nitric acid in **93**?

d. Will other acids behave like sulphuric acid? Mix some pulverized sodium nitrate with phosphoric acid, agitate for a minute or two, and apply the copper test as in *a* (?). Could phosphoric acid be used in the preparation of nitric acid as in **93**? Why? Could hydrochloric acid be used [R 182, 440, 448]? Could hydrofluoric acid be used [R 241, 440]? Give reasons for your answers.

97. Properties of Nitric Acid.

a. If **93** was performed, note the color of the sample (?). Blow some air from the blast through the acid (?). What is the color of pure nitric acid? To what substance was the color of this sample due, and by what action was it formed? What property of nitric acid does its formation indicate? Blow the moist air of the breath over this specimen (?). What property does this indicate? Determine the boiling-point of anhydrous nitric acid by boiling this sample in a distilling-flask with a thermometer immersed in the vapor (?).

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b. Test dilute nitric acid with litmus paper (?).

c. Add 1 g. of sulphur to 2–3 c.c. of concentrated nitric acid and boil [Hood] for two or three minutes (?). Is there any evidence of action? Pour the clear liquid into another test-tube, dilute with water, and test for the sulphate radical (?). What property of nitric acid is here shown?

d. The interaction of dilute (**16** *c*) and of concentrated (**16** *d*) sulphuric acid with metals has already been studied. Try the action of (a) magnesium and (b) zinc, separately, either upon dilute or upon concentrated nitric acid, and of (c) copper upon both, and explore the whole action thoroughly in each of the four cases as follows:

Fit up a side-neck test-tube with a dropping-funnel passing through a perforated cork, and attach a delivery tube (or use an ordinary test-tube with cork and delivery tube). Place a small amount of the metal in the tube and admit the acid from the dropping-funnel. After the air has been displaced, collect the gas over water in a test-tube inverted in the pneumatic trough (or in an evaporating-dish).

If the gases in the generating tube remain colored, nitrogen tetroxide is present. If the gas is at first colored, but becomes colorless, nitric oxide is present: confirm by admitting air to the tube in which it has been collected (?). Hydrogen, if liberated alone, would show neither of these properties, but might be identified by its inflammability (?). If both hydrogen and nitric oxide are liberated, why may we not feel confident of being able to cause the former to burn when thus diluted? How can the nitric oxide be separated (**94** *d* or *e*) so as to leave the hydrogen in an inflammable condition? Examine the gas in each case for these three substances.

If ammonia is formed in any of these four cases by complete reduction of the nitric acid, where will it be found, and in what condition? (Consider all the circumstances carefully, or you will answer wrongly.) Test for its presence (**92** *d*) (?). Evaporate on a water bath [Hood] the solution remaining in the test-tube after any one of these experiments (?). Collect the residue and heat it in a dry test-tube (?). In what form of combination was the metal (**95**)?

e. Grasp a test-tube by means of a strip of folded paper (Fig. 5, p. 14), place in it a piece of granulated tin, and add some concentrated nitric acid (?). When the action has exhausted itself, add much water and boil. Fit a small filter paper carefully into a funnel [Note 24, p. 9], collect the solid product upon the filter and wash [Note 38, below] precipitate and paper with water. Test the filtrate as it runs through to see whether it becomes

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neutral (?). Spread the filter paper with the precipitate upon a water bath or radiator to dry and ascertain as in **95** whether the product is a nitrate (?). Why would the test in **94** *g* be unsuitable here?

f. Comparing dilute and concentrated nitric acid with the same forms of sulphuric acid, what points of resemblance and of difference have you observed?

Account for the differences in the actions of dilute and of concentrated nitric acid in *c*, *d*, and *e*, in respect to the gaseous product of reduction which is typical of each.

g. Dip a piece of wool in concentrated nitric acid, or note the nature of the products formed when the acid falls upon the hands or clothing (?). Would cotton behave in the same way? Explain [R 441].

h. To 1–2 c.c. of nitric acid add 3–4 c.c. of pure, concentrated hydrochloric acid, warm gently, and note the appearance and odor (?). Will these acids, singly, attack all metals? Explain (?). What metals are attacked only by the mixture (*aqua regia*), and why? What form of combination do the metals assume?

Note 38.—In filtering, observe the directions in Note 24. **To wash a precipitate** first let the mother liquor drain away completely and press the precipitate with a spatula. Then cover the contents of the funnel, including the whole paper (why?), completely (and repeatedly, if necessary) with the washing material. When the washing is complete, dry the product by pressing with dry filter paper.

98. Nitrous Oxide.

a. In a test-tube or small flask provided with a cork and delivery tube (Fig. 10, p. 24), place 10 g. of ammonium nitrate. Heat cautiously with a small flame [Care!], and, after the air has been expelled, collect the gas in two bottles over water (warm water, if available. Why?). Why is the stream of gas so slow, relatively to the vigor of the action? What are the relative volumes of the products at 100° ?

b. Into one bottle lower a glowing splinter of wood (?).

c. Into the other bottle lower a deflagrating spoon containing a very little burning, red phosphorus (?). If this experiment were to be conducted in a closed vessel, what, if any, change in pressure would be observed after the products had cooled?

99. Nitrates.

a. How does lead nitrate behave when heated? What other nitrates behave like it? How does ammonium nitrate behave when heated?

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b. Take 2–3 g. of sodium nitrate in a hard glass test-tube; and heat strongly and persistently until the evolution of gas ceases. Test the escaping gas for oxygen. Use the residue in **100** *a*. What nitrates behave in this way when heated?

100. Nitrites and Nitrous Acid.

a. When the residue from **99** *b* has cooled, add not more than 3 c.c. of water, shake vigorously until the whole has dissolved, and divide into three parts. To one portion add dilute sulphuric acid (?). How could a nitrite be distinguished from a nitrate?

b. To 5 c.c. of starch emulsion add a drop of potassium iodide solution and some dilute sulphuric acid, and then introduce a little of the solution from *a* (?).

c. Dilute 1–2 c.c. potassium permanganate solution with a large excess of dilute sulphuric acid, and add a drop of this mixture to the solution from *a* (?). The actions in *a*, *b*, and *c* serve for the detection of nitrites and nitrous acid. What other characteristic property of nitrites has been encountered (**90** *a*)?

d. Examine now the solution obtained by leading nitrogen tetroxide into sodium hydroxide (**95**). Take a portion of the solution and acidify (test?) with dilute sulphuric acid (?). To the mixture add a drop of diluted potassium permanganate solution (?) or some starch emulsion containing a drop of potassium iodide (?). What substance was present?

To ascertain whether this alkaline solution contains a nitrate as well as a nitrite, the latter must first be eliminated. To the remainder of the alkaline solution, transferred to a small flask, add at least 5 g. of ammonium chloride [Hood] and heat to boiling (?). Explain the evolution of ammonia. What other gas is given off (**90** *a*)? When the action is entirely over, add about 10 c.c. of water, and shake. Prepare 2–3 c.c. of a concentrated solution of ferrous-ammonium sulphate [Note 37, p. 68] (or of ferrous sulphate), add to it 1–2 c.c. of the solution to be examined, and complete the test for a nitrate described in **94** *g* (?). Write now the equation for the action of nitrogen tetroxide on sodium hydroxide.

101. Active (Nascent) State of Hydrogen. Dilute some potassium permanganate solution with water, and add an equal volume of dilute sulphuric acid to it. Divide into two parts. Through one pass a stream of hydrogen gas from the laboratory supply or from a Kipp's apparatus (?). To the second add some zinc dust, and shake (?). Interpret the result.

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CHAPTER XIV.

PHOSPHORUS.

102. Phosphorus. What difference in general chemical behavior do the two allotropic modifications of phosphorus exhibit [R 459]? What product is formed when phosphorus burns in excess of oxygen, and what is formed when the oxygen is limited in amount [R 464]?

103. Phosphine [Hood]. Place a very small piece of calcium phosphide in a little water in a beaker (?). What mode of forming ammonia is similar to this, and how is it similar? Repeat, using dilute hydrochloric acid instead of water (?). What mode of forming hydrogen sulphide is similar to this, and how is it similar? In what ways does phosphine differ from ammonia [R 461]? Which of the differences are shown in these experiments? Why should we expect ammonia and phosphine to be alike? Test with litmus the water in which the calcium phosphide was placed (?), and explain.

104. Metaphosphoric Acid.

a. Throw 2 g. of phosphorus pentoxide, in minute portions at a time, into a beaker containing 10 c.c. of cold distilled water (?). Allow the liquid to stand for a few minutes, or until clear. Test the liquid with litmus paper (?). What acid is present [R 464]? Use the solution for *b* and *c* and **105** *a*. Why could not the product made by burning phosphorus in a closed volume of air be used in this case?

b. To a part of the solution from *a* add silver nitrate solution, a little at a time, shaking between additions, until a permanent precipitate (color?) is formed (?). Is an action like this reversible? Is this action incomplete? To answer, add one or two drops of diluted (1 : 4 Aq.) ammonium hydroxide solution, observe whether the precipitate increases, and explain. This is a reaction of what ion? What other substances would give it?

c. To 1 c.c. of albumen solution, add one or two drops of the solution from *a* [R 468] (?). This is a reaction of the free acid only, and not of metaphosphate-ion.

105. Orthophosphoric Acid.

a. Dilute the remainder of the solution of metaphosphoric acid from **104** *a* with 10 c.c. of water, and boil in a small flask vigorously for an hour or more. If necessary add more water

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to make up for the loss by evaporation. Cool the solution, treat portions of it with silver nitrate and with albumen, as in **104** *b* and *c*, and answer the same questions. How may the formation of this acid, during the boiling, be hastened [R 465]?

b. Heat 1 g. of red phosphorus with 5 c.c. of slightly diluted nitric acid in a test-tube (?). When the action has ceased, filter, if necessary, and drive off the water and excess of nitric acid completely by evaporation [Hood] on a water bath. Mix with a few drops of concentrated nitric acid the syrup which remains, and evaporate once more. It is essential that all the nitric acid be finally removed (why?). Redissolve the syrup in water and test with litmus paper (?).

Treat part of the solution with silver nitrate as in **104** *b*, and answer the same questions (a black precipitate with silver nitrate is due to phosphorous acid [R 469] formed by incomplete oxidation).

c. Take 5 c.c. of the solution of ammonium molybdate in nitric acid [Side-shelf], add to it two drops of the solution of orthophosphoric acid prepared in *b*, and warm gently (?). This is a very delicate test for phosphoric acid, or orthophosphate-ion.

106. Phosphates.

a. Take some sodium phosphate (secondary sodium orthophosphate) solution and test it with litmus paper (?). What ions are present? Are acid salts always acid towards litmus (**74** *b*)? If not, explain why they are not. Explain also the actual reaction of this solution.

b. To a small part of the sodium phosphate solution add silver nitrate solution until the precipitation is complete (?). What is the precipitate (see **105** *a* and *b*)? What are the reactions towards litmus of the sodium phosphate (*a*), and silver nitrate solutions singly? Test the mixture with litmus paper (?). What ion is evidently formed, and what product is therefore present?

c. Prepare a little "magnesia mixture" by adding to 1 c.c. of magnesium sulphate solution a few drops of ammonium hydroxide and then excess of ammonium chloride solution. Add to the rest of the sodium phosphate solution a little of this mixture (?). In making the equation, disregard the ammonium chloride, which is added only to prevent precipitation of magnesium hydroxide. This is another test for the presence of what ions?

d. Strongly heat [Blast-lamp] 2 g. of dry sodium phosphate in an open crucible for twenty minutes, or until no further change is observed (?). Dissolve the cold mass in water (it

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dissolves very slowly), and test a portion of the solution with silver nitrate solution (?). This is a reaction of what ion? Take the remainder of the solution, liberate the acid (?) by adding acetic acid, and introduce a few drops of the liquid into a solution of albumen (?).

Make a table showing the effects of the three phosphoric acids upon albumen and the colors of their silver salts. How could you identify salts of the three acids?

e. Heat strongly [Blast-lamp] 2 g. of microcosmic salt as in *d*. Note the odor (?) and reaction towards moistened litmus paper (?) of the vapors given off. Dissolve the residue in cold water and use the tests tabulated in *d* to learn what salt has been formed.

f. Make a bead on a straight platinum wire as in **3** *c*, using microcosmic salt instead of borax. Of what must the bead consist? Now fuse with it (**3** *d*) a minute particle of cupric oxide (?). What difference do your experiments show as to the relative stabilities of $NaPO_3$, $NaNO_3$ (**99** *b*), and $KClO_3$ (**15** *a*)?

107. Halides of Phosphorus.

a. What were the actions of water on the tribromide (**44** *b*) and tri-iodide (**48** *b*) of phosphorus?

b. Place 2–3 c.c. of phosphorus trichloride in a dry test-tube and blow the breath over the tube (?). Add water drop by drop (?) until about 5 c.c. has been used, then boil the solution (Fig. 5, p. 14). Test the vapor with litmus paper (?) and with a rod dipped in ammonium hydroxide (?). Evaporate [Hood] the solution to a syrup on the water bath (?).

c. Transfer part of the syrup from *b* to a small test-tube and heat until the gas evolved may be ignited at the mouth of the tube (?). Note the odor of this gas before igniting it (?). Continue heating until the action is over. Ascertain according to **106** *d* which of the phosphoric acids constitutes the residue (?).

d. Dilute 1 c.c. of potassium iodide solution with water and dissolve in the liquid a crystal of iodine. Add to this solution a little of the syrup from *b*, and shake (?).

e. Place upon a watch-glass 5 or 6 small granules of phosphorus pentachloride and blow the breath over them (?). Throw them into 2–3 c.c. of water in a test-tube (?) and boil. Test the solution with litmus (?). To a small part of the cold solution add excess (test?) of silver nitrate solution (?). Filter. What remains upon the paper (?). To the filtrate add diluted (1: 4 Aq.) ammonium hydroxide drop by drop (shake between drops) (?).

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CHAPTER XV.

CARBON.

108. Charcoal.

a. Place a small piece of charcoal in a test-tube half full of water (?). Now hold it under the water with the reverse end of the file, and boil the water for several minutes (?). When the whole has cooled, test once more the tendency of the charcoal to float (?). Explain.

b. Boil dilute solutions of litmus and indigo, separately, with pulverized animal charcoal, and filter each liquid (?). The activity of the charcoal is much increased by previous heating in a covered crucible.

c. Fit a hard glass test-tube with a cork and L-tube. Mix intimately in the mortar 1 g. of pulverized cupric oxide with 1 g. of pulverized wood charcoal and place in the tube. Heat persistently [Blast-lamp] and pass the gases through 5 c.c. of lime-water (?). Examine the residue by rubbing vigorously under water in the mortar and washing away the lighter particles (?). What property of carbon is here illustrated?

109. Carbon Dioxide.

a. Place a few small pieces of magnesite (magnesium carbonate) in a hard glass test-tube fitted with a cork and L-tube and heat strongly. Pass the gas through 5 c.c. of lime-water in a test-tube (?). What is the residue [R 643]?

b. Fit up a generating-flask (Fig. 8, p. 20) and connect with two wash-bottles (Fig. 18, p. 69) containing water and concentrated sulphuric acid, respectively (what is the use of each of these? The latter is unnecessary if **110** is omitted). Place in the flask some pieces of marble and pour upon them diluted hydrochloric acid. Collect the gas in two bottles by downward displacement.

What substances could be substituted for marble in this experiment? What other sources of carbon dioxide have been encountered (**13** *c*, **108** *c*, **109** *a*; see also **111** *a* and *c*, **113** *b*, **114** *b*, **118**)?

c. To one add a little water, close with the hand, and shake (?). Is the gas soluble in water, or not?

Use the second to compare its weight with that of air. Employ baryta-water as a test.

d. Take two test-tubes containing distilled water, pass a

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current of the gas into one, and test each with litmus paper (?). Boil the solution, and test again with litmus (?). Explain.

e. Lead the gas into a little sodium hydroxide solution in a test-tube until the solution is saturated (test? Note 36, p. 67). Let the solution stand until it dries spontaneously (first residue). Heat the dry residue (?) in a test-tube, and determine what two things are given off.

To this residue after heating (second residue) add dilute hydrochloric acid until all action (?) ceases. Evaporate the solution on the water bath, and examine and taste this final residue (?). Having recognized the products of the last action, and taking into account the preceding observations, state what the nature of the second and first residues must have been. Write equations for all actions.

110. Molecular Weight of Carbon Dioxide [Quant.].

a. Determine the weight of a measured volume of the gas by the method used for sulphur dioxide (**78**), and calculate the weight of the gram-molecular volume. What further information must we have to enable us to determine the formula?

b. Use the quantitative results obtained in the synthesis of carbon dioxide (**34**) along with this molecular weight, to calculate the weights of carbon and of oxygen in a molecular weight of the gas. What further steps are necessary in order to fix the atomic weight of carbon?

111. Carbon Monoxide.

a. Heat about 10 g. of oxalic acid crystals with concentrated sulphuric acid in a generating-flask (Fig. 8, p. 20), and fill a bottle over water with the gas which is given off. Shake with lime-water (?). With what substance should we wash the gas to remove the carbon dioxide? Arrange a wash-bottle to purify the gas. Fill two bottles with the purified gas over water. Test one with lime-water again (?). If the gas is pure, burn that in the other bottle, add lime-water at once, close quickly, and shake (?).

b. Devise a way of ascertaining roughly the relative volumes of the two gases generated in *a*, and measure the proportion in a test-tube full of the mixed gases.

c. Pass a stream of the purified carbon monoxide over a little pulverized cupric oxide, heated in a boat in a hard glass tube (?). What gas is formed? What remains in the boat? What is here the reducing agent?

112. Molecular Weight of Carbon Monoxide [Quant.]. Obtain [Storeroom] a round-bottomed, 250 c.c. flask. Fit it with a rubber stopper through which passes a short, straight tube. Attach to the latter a short piece of rubber tubing

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closed with a strong pinch clamp. Make a mark on the neck at the bottom of the stopper, so as to be able to measure the exact content of the flask up to the stopper. Place 30 c.c. of water in the flask, insert the stopper, remove the clamp, and boil the water with a small flame for about five minutes, so as to drive out all the air. Close the rubber tube with the clamp and remove the flame quickly, wipe the flask and allow it to cool. When it has assumed the temperature of the air, weigh the whole carefully, suspending the flask on the balance by a thread tied round the neck. Connect with the apparatus delivering pure carbon monoxide, and open the clamp a very little so as to admit a slow stream of the gas. When the flask is full, close the clamp, disconnect from the generating apparatus, open the clamp for an instant to restore the pressure to that of the atmosphere, and weigh again. The gain in weight represents the weight of the carbon monoxide. Read the barometer and thermometer. Subtract from the barometric reading the aqueous tension at the observed temperature. Ascertain the volume of the flask by filling with water to the mark and weighing again.

Calculate the weight of the G.M.V. of the gas.

To what class of gases would this method of determining the density and molecular weight be applicable? Why could not this method be used for carbon dioxide?

113. Methane (Marsh Gas).

a. Pulverize about 5 g. of fused sodium acetate and about 20 g. of soda-lime (a mixture of quicklime and sodium hydroxide). Mix the ingredients intimately in the mortar, and place in a large test-tube fitted with a one-hole cork and delivery tube (Fig. 6, p. 15). Rap the test-tube gently so as to form a space for the passage of the gas. Then clamp the tube close to the cork in a slightly inclined (5°) position, so that it slopes toward the mouth (why?). Slip over the tube a cylinder of wire gauze, and, beginning at the rear or sealed end, heat the contents gently until the evolution of gas is uniform. When all the air is displaced, collect one bottle of gas over water.

Attach a small nozzle to the end of the delivery tube and ignite the gas. Note the color and degree of luminosity of the flame (?). Hold over the jet a dry inverted beaker and observe one product of the combustion (?).

b. Hold the bottle containing the gas mouth downward and apply a light (?). Quickly pour into the bottle some lime-water, and shake (?). What volume of oxygen is required for the complete combustion of one volume of methane, and what

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ratio will the resulting volume of gases bear to the original volume of methane, at 0° and at 100°, respectively?

114. Ethylene [Hood].

a. Fit a 250 c.c. flask with a doubly-bored cork, through which pass a dropping-funnel and L-tube. Attach a gas-washing bottle containing a little water, and connect an L-shaped delivery tube. Test the apparatus to see that it is air-tight. Place in the flask about 20 c.c. of phosphoric acid, and clamp it to a ring-stand over a sand bath. Introduce into the bulb of the dropping-funnel (or substitute, **36** *b*) some alcohol. Finally, heat the phosphoric acid, and when it has had time to reach 220°, admit the alcohol drop by drop beneath the surface of the phosphoric acid in the flask.

b. Fill a bottle with the gas over water and apply a light (?). Quickly pour some lime-water into the bottle, and shake (?). Attach a nozzle to the exit tube of the washing-bottle and raise the other tube clear of the water (why?), ignite the gas, and observe the luminosity of the flame. What commercial use has ethylene [R 513]? Hold a cold, dry beaker over the flame (?). What are the products of complete combustion of all hydrocarbons?

c. Detach the nozzle, reattach the delivery tube to the exit tube, and lower the other tube of the washing-bottle once more. Place 1 c.c. of bromine [CAUTION!] in a test-tube, cover it with 5 c.c. of water, put the test-tube into a beaker filled with cold water, and allow the gas to bubble into the bromine. When the color of the bromine has disappeared, examine the contents of the test-tube (?). Is the product colored? Is it soluble in water? What do you infer as to its specific gravity? Detach the dropping-funnel, wash it out, and place in it the contents of the test-tube. Draw off the lower, oily layer into a dry test-tube and note its odor (?). Try its solubility in alcohol (?).

Why is the accepted formula for ethylene preferred to the simplest? What volume of oxygen would be required to burn one volume of the gas completely? What would be the relative volumes of the products at 0° and 100°, respectively? What volumes of bromine vapor and ethylene would be required for complete combination, and what would be the relative volume of the product (in the state of vapor)?

115. Acetylene. Fill a test-tube with water and invert it in water in an evaporating-dish. Introduce a small piece of calcium carbide under the mouth of the tube (?). Test the water with litmus (?). Bring a light to the mouth of the tube (?). Note the luminosity of the flame, and compare with flames of methane and ethylene (?).

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Can you state a general method for making hydrides of non-metals (such as C_2H_2, PH_3, NH_3)? Can SH_2 [R 645] and ClH [R 715, 718] be formed similarly?

116. Illuminating-Gas.

a. Heat some sawdust in a dry test-tube (?). Note the odor (?), reaction towards moist litmus paper (?), and combustibility (?) of the vapors. What is the residue?

b. Repeat *a*, using bituminous coal (?).

c. Pulverize a few particles of potassium sulphate. Take a small Bunsen flame and reduce the supply of air until a small luminous region appears. Heat the platinum wire, touch the salt with it, and hold the adhering powder steadily in the luminous part. After a minute or two, withdraw the bead, place it upon a clean silver coin and moisten with a drop of water (?). Explain the result. What are the reducing agents used here?

117. Acids.

a. To 1 g. of sodium acetate add some dilute sulphuric acid, and warm. Note the odor (?). How could you use this action to make acetic acid? How is it manufactured [R 498]?

b. Take 5 c.c. of acetic acid. Test with litmus paper (?). Recall its interaction with zinc or iron (**16** *e*) (?). To the acid add 3–4 g. of litharge and boil gently for a few minutes (?). Filter, if necessary, while hot, and set the clear solution aside to crystallize (?). What is the common name of the product [R]?

118. Alcohol. Dissolve 20 g. of glucose syrup in 150 c.c. of water and add yeast. Fill a flask to the base of the neck with the mixture, tie a piece of filter paper over the mouth with thread [Side-shelf], and set the whole aside in a warm place for 3–4 days. Then warm the solution and test the gas which is given off for carbon dioxide (?).

Filter the liquid and place it in a larger flask, fitted with a cork and L-tube, and connect (Fig. 14, p. 45) with a condenser [Storeroom]. Distil off about 50 c.c. Place the distillate in a distilling-flask [Storeroom] fitted with a thermometer, boil with a small flame, and catch the part which passes over between 75° and 93°.

Note the odor of the distillate (?). Test it with litmus paper (?). Use one drop to ascertain whether it burns. To the rest add a crystal of iodine and enough sodium hydroxide solution to dissolve it. Shake vigorously, and do not add more alkali than is absolutely necessary. Warm the solution and then cool it (?). This is the iodoform test for alcohol.

119. Esters.

a. To 1 g. of sodium acetate add 1–2 c.c. of alcohol and 1 c.c. of concentrated sulphuric acid. Warm, if necessary, agitate

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for a minute or two, and note the odor (?). This is a test for acetic acid or an acetate.

b. Place in a porcelain dish a piece of fat the size of a pea, and add 4 c.c. of alcohol and five drops of a 50 per cent solution of sodium hydroxide (made with 1 g. of the solid and 1 c.c. of water). Stir constantly and boil very gently until the odor of alcohol is no longer perceptible, then stop. The alcohol is used as a common solvent for the fat and the alkali. What is the residue [R 505]?

Dissolve the soap in hot water, cool, and to half of the solution add dilute hydrochloric acid, and shake vigorously (?). Withdraw the floating coagulum by means of a glass rod, suspend it in water in a test-tube, add a few drops of sodium hydroxide, and heat until solution takes place. What do you conclude from its solubility in the alkali?

To the other half of the soap solution add calcium chloride solution (?). Explain the action of hard water [R 594] on soap solution.

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CHAPTER XVI.

THE ACTIVITY OF ACIDS MEASURED CHEMICALLY.

120. Estimation of the Relative Activity of Acids. Characterize briefly some of the methods available for measuring the relative activity of acids [R 679].

a. When methyl acetate is mixed with water, it undergoes hydrolysis very slowly, acetic acid and methyl alcohol being formed: $CH_3.C_2H_3O_2 + H_2O \rightleftarrows CH_3OH + HC_2H_3O_2$. Add about 1 c.c. of methyl acetate to 10 c.c. of distilled water in a test-tube, test with litmus paper (?), and cork up and label the mixture. After several days, test once more with litmus (?).

This action of water is found to be greatly hastened by the addition of free acids, although the acids remain themselves unchanged by the process. Equivalent quantities (?) of different acids show very different accelerating powers toward this reaction. The order in which they are placed by measurement of this particular form of activity, however, is the same as that into which they fall when compared by any of the other methods. The extent to which the change has taken place can be measured at any moment by titration with alkali. The quantity of acid which was present at starting being known, the quantity found is the same acid plus the acetic acid set free by the progress of hydrolysis. Subtraction gives the quantity of the latter, and this quantity is a measure of the activity of the accelerating acid. The activities of hydrochloric and sulphuric acids are compared in *b* by this method.

b (Two students working together). Procure two 20 c.c. stoppered, graduated flasks,* and a 10 c.c. and a 1 c.c. pipette [Storeroom]. Mark the flasks with a file so as to be able to distinguish them, and into one measure exactly 10 c.c. of normal (?) hydrochloric acid, and into the other 10 c.c. of normal (?) sulphuric acid. Put exactly 1 c.c. of methyl acetate into each, and fill both flasks with distilled water up to the 20 c.c. mark at once (why at once?). Stopper the flasks tightly, mix the contents, and suspend both so that their necks are just above the water in a large bath (use the pneumatic trough) heated to

* Instead of graduated flasks, common flasks with cork stoppers may be used. Measure into each flask 10 c.c. of acid and then, with the same pipette, 10 c.c. of water. Add the 1 c.c. of methyl acetate, shake, and proceed as directed.

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about 45°. If the bath is fairly large, further external heating will not be necessary. Otherwise, maintain the temperature by means of a small flame. In accurate work the temperature must be kept constant within 0.1° during the experiment by means of a thermostat. Allow the flasks to remain in this position for 30 minutes (t).

While this is going on make some normal (or approximately normal = 4 per cent) sodium hydroxide and fill a burette with it. Take fresh portions of 10 c.c. of each of the acids and titrate them with the alkali, using two drops of phenolphthaleïn as an indicator. Record the results. These numbers measure the amount of mineral acid, at starting, in each flask.

When the above time has elapsed, remove both flasks from the bath, transfer the contents of each to a separate beaker, rinsing out the flasks with distilled water. Add two drops of phenolphthaleïn to each portion and titrate with the solution of sodium hydroxide used before. The difference (d) between the volumes of alkali required for the neutralization of 10 c.c. of each acid with and without methyl acetate represents the amount of sodium hydroxide required to neutralize the acetic acid liberated in the hydrolysis. The two values of d obtained are functions of the activity of the acids. Which acid is more active? What, according to the theory of ionization, is really measured in these experiments? What does the result of a show water to be?

Calculate S, the speed with constant, unit concentration, by the formula for a unimolecular action [R 252]. The initial concentration (c_1) of 1:20 is equal to 0.67 moles per liter. The proportion transformed (x), which must be expressed in the same units, is $d/20$ moles per liter. Then $S = 1/t \log_e \{c_1/(c_1 - x)\}$. The ratio of the values of S for the two acids defines their relative activities. The time (t), being the same for both, may be neglected, and common logarithms may be used, because the factor for converting them to $\log_e$ (2.3025) cancels in the ratio.

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CHAPTER XVII.

SILICON AND BORON.

121. Silica. Mix 1 g. of finely powdered silica with 4–5 g. of anhydrous sodium carbonate. Make a small watch-spring spiral on the end of the platinum wire, and, by alternately heating in the Bunsen flame or blast-lamp, and dipping in the mixture, obtain a large bead and heat it strongly till all action (?) seems to have ceased. Place the bead in a test-tube and make others by the same process. Dissolve the beads in a small amount of water. Add hydrochloric acid a drop at a time until the solution is strongly acid (?). Evaporate the solution to dryness on the sand bath (?). Treat the residue with warm water, wash the whole contents of the dish into a test-tube, and examine (?).

122. Analysis of a Silicate. Mix dry potassium carbonate with anhydrous sodium carbonate in equal proportions in a mortar. Coil the platinum wire to watch-spring form. Mix a little powdered talc (is this soluble in water? What is its common name?) with 6–7 times as much of the "fusion mixture," and hold some of the result on the platinum wire in the flame of the blast-lamp till it is completely melted and all action (?) has ceased. Repeat till several beads are obtained. Treat the beads with boiling water in a test-tube until they are completely disintegrated. Filter through a small filter paper and wash the precipitate with water. Preserve this filter paper and precipitate for use later. Acidify the filtrate with concentrated hydrochloric acid and proceed as in **121.**

Make a hole in the paper and wash the precipitate obtained above into a test-tube. Add dilute hydrochloric acid, and warm (?). Filter, if necessary, and add ammonium hydroxide to alkaline reaction (?). The precipitate is aluminium hydroxide. Boil and filter. To the filtrate add a few drops of ammonium hydroxide, some ammonium chloride solution, and some sodium phosphate solution, and shake (?). Compare **106** *c*.

123. Silicon Tetrafluoride. Mix intimately 1 g. of pulverized calcium fluoride with an equal weight of sand, place in a test-tube, and moisten the mixture with concentrated sulphuric acid. Apply a gentle heat (?). Hold a glass rod, with a drop of water at its lower end, in the gas and examine the rod (?).

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124. Boric Acid.

a. Pulverize some borax and make a strong solution in boiling water. Add concentrated hydrochloric acid until the solution is strongly acid, and set aside to cool (?). Filter off the crystals, wash with a few drops of cold water [Note 38, p. 85], and dry. Dissolve the crystals in the smallest possible amount of boiling water, and set the solution aside (?). Filter, and wash the crystals as before.

b. Dissolve a part of the crystals in hot distilled water. Test this solution, and a sample of the distilled water, simultaneously with litmus paper (?). Dip a strip of turmeric paper in the same solution, wrap it round the upper part of the test-tube, and boil the solution until the paper is dry (?). Touch the paper with a glass rod dipped in sodium hydroxide solution (?). This is a test for boric acid.

Treat the rest of the crystals with cold sodium hydroxide solution (?).

c. Place on separate parts of a watch-glass a drop of concentrated sulphuric acid, a drop of glycerine, and a very little pulverized borax. Rub the end of a platinum wire in each of these. Bring the end of the wire slowly up to the outer edge near the bottom of a small Bunsen flame. How is the flame colored? This is a test for a borate.

An alternative method: Dissolve a small crystal of borax in 1–2 c.c. of water in a test-tube. Add a drop or two of concentrated sulphuric acid and then 2–3 c.c. of alcohol. Heat the mixture and set fire to the vapor of the alcohol.

125. Borates.

a. Dissolve 1 g. of borax in distilled water. Test both this solution, and the distilled water, with litmus paper (?).

Put two drops of the solution into a test-tube and dilute with water till the tube is two-thirds full. To the remainder add silver nitrate solution (?). Add silver nitrate solution to the very dilute solution also (?). The difference is more marked if the dilute solution is first warmed. For comparison, add silver nitrate solution to an exactly equally diluted sodium hydroxide solution (?). What conclusion do you draw in regard to the action of water on borax? Write the equation, and explain.

b. Heat a straight platinum wire in the Bunsen flame, and, while yet glowing, dip it into a small quantity of borax. Return the wire to the flame and observe the changes in the substance (?) until it forms a bead. Try borax beads, as directed in **3** *d*, *e*, and *f*, with cupric oxide (?), manganese dioxide (?), and ferric oxide (?), separately.

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CHAPTER XVIII.

METALLIC ELEMENTS OF THE ALKALIES.

126. Potassium Hydroxide.

a. Dissolve about 30 g. of potassium carbonate [Notes 10, 11, 12, p. 2] in 200–300 c.c. of water in a large beaker, and heat on a wire gauze to boiling. Slake 15–20 g. of quicklime in a beaker (?), using heat if necessary to start the action, and make the product into a very thin paste with water. Add this gradually, and with constant stirring, to the boiling solution (?). Continue boiling for a few minutes (why?). Let the mixture settle, and, when it is cold, decant the clear liquid (or filter rapidly). Use the solution in *b*, *c*, and *d*.

Is calcium hydroxide appreciably soluble (Appendix IV)? Is calcium carbonate more or less soluble than is the hydroxide? Formulate the action and explain why it went to completion. What kind of hydroxides alone can be made by this method [R 553]? Which hydroxides are of this kind (Appendix IV)?

b. Find the strength of this solution by titration (alkalimetry). To do this, place a carefully measured volume (about 10 c.c.) of the clear solution in a small flask. Dilute with about four times its volume of water, as the concentrated solution is apt to decompose the indicator. Fill a burette with "normal" [R 148] hydrochloric acid * [Side-shelf]. Add some phenolphthaleïn solution to the alkali and run in the acid cautiously until the red color just disappears. Note the volume of acid used. Calculate the weight of potassium hydroxide per liter, which your measurement shows to be contained in the alkaline solution. Express this also in terms of a normal solution containing 56 g. of KOH per liter (for example, 28 g. per liter would be 0.5 normal).

c. (Two students working together). If the alkaline solution is above normal, calculate the volumes of water and of the solution required to make 100 c.c. of normal alkali. Place the necessary amount of water (by weighing) in a 100 c.c. graduated

* Or normal oxalic acid may be prepared (two students working together), and used here. Calculate the weight of pure [Instructor] oxalic acid [R 499] required to make 500 c.c. of normal oxalic acid solution [R 148]. Weigh out [quant.] this amount on glazed paper, and transfer it to a 500 c.c. graduated flask [Storeroom]. Dissolve the acid in distilled water and then fill up the flask to the mark.

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flask [Storeroom] and fill to the mark with the solution. (If the solution is less than normal, calculate and use the amounts required for 200 c.c. of semi-normal alkali.)

Measure (burette) 5 c.c. of acetic acid into a flask and dilute with about 20 c.c. of water (or take 25 c.c. of commercial vinegar), add phenolphthaleïn, titrate with the normal (or semi-normal) alkali, and calculate the percentage of acetic acid present.

d. Place very small quantities of the following solutions in separate test-tubes, dilute with water, and add excess of the solution of potassium hydroxide from *a* to each; ferric chloride (?); cupric sulphate (?); mercuric chloride (?). Describe the color and structure of the precipitates [Note 39, below]. Boil the contents of each test-tube (?). Do the precipitates dissolve or change in any way?

What kind of hydroxides can be made by this method? Do any metals fail entirely to form hydroxides [R 541]?

e. Pulverize a small piece of potassium hydroxide and leave it exposed to the air on a watch-glass for 24 hours, or more (?). To a part of the product add dilute hydrochloric acid (?). Simultaneously, treat a small piece of sodium hydroxide in exactly the same way (?). Compare the results and explain.

Note 39. — The **structure of a precipitate** may be described as gelatinous, flocculent, curdy, pulverulent, granular, or crystalline. What circumstances will determine the structure of a precipitate? Hereafter, describe every precipitate by terms like these.

127. Potassium Nitrate.

a. Dissolve 25 g. of sodium nitrate and 22 g. of potassium chloride in 50 c.c. of water and evaporate to half the volume on the sand bath. Fit a filter paper into a small funnel [Note 24, p. 9]. As rapidly as possible decant the hot, clear liquid from the crystals and set it aside. Throw the crystals which appeared during boiling at once on to the filter, and rapidly press out the rest of the mother-liquor with a spatula. Examine the form of the crystals and ascertain what they are (?). (If they are too small, recrystallize a part slowly from water in a beaker in order to learn their form.) When the decanted liquid is cold, press the product on a filter likewise. Examine this set of crystals as before (?). Compare both with the original substances.

To understand the process, note the solubilities (grams dissolved by 100 g. water) of the substances concerned (Appendix V):

	10°	100°		10°	100°
Potassium nitrate		246	Potassium chloride		
Sodium chloride			Sodium nitrate		

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Which of these substances will first be deposited from the boiling liquid? Ascertain by calculation how much of it (roughly) will be deposited at 100°, how much more will come out when the liquid cools, and how much will remain in the mother-liquor. What other substance will be present in large quantity in the hot mother-liquor, and how much of it must there be? How much of this product will be deposited when the liquid cools, and how much will be lost by remaining dissolved? What per cent of the possible yield of potassium nitrate may we expect to get? Dry your product, weigh it, and calculate what per cent was secured.

Explain why purer potassium nitrate can be obtained by crystallizing the product once more from water.

b. Mix intimately in the mortar 5 g. of finely pulverized potassium nitrate with 2 g. of charcoal, and drop the mixture in small portions into a red-hot crucible (?). What gases are evolved? What is the residue (test with an acid)?

c. Pulverize 5 g. of potassium nitrate and mix on paper [CAUTION] intimately with 2 g. of flowers of sulphur. Throw the mixture [Hood] in small portions into a red-hot crucible (?). What gases are evolved? Dissolve the residue and add barium chloride solution (?). Explain the explosive power of gunpowder (?).

128. Potassium Cyanide [POISON]. How is this salt made [R 558]? Place 2 c.c. of potassium cyanide solution in an evaporating-dish, heat it, and add yellow ammonium sulphide solution until the color (?) no longer disappears. Evaporate to complete dryness [Hood]. Dissolve a part of the residue with water, and add ferric chloride solution (?). A black precipitate (?) indicates that the heating was not sufficient. If this appears, heat the residue once more and try the action of ferric chloride again. In the first part of this experiment, what property of the cyanides [R 507], and which kind of ionic chemical change, are illustrated? Is this change instantaneous, as is the union or disunion of ions?

129. Reactions of Potassium Salts.

a. Heat a little solid potassium nitrate on a clean platinum wire. Notice the color of the flame and examine with the spectroscope. Make a diagram showing the position of the lines with reference to the D line (in the yellow), which, on account of the sodium present, is shown by all flames in the laboratory.

b. Saturate 10 c.c. of warm water (40°) with potassium nitrate. Add this solution to an equal volume of tartaric acid solution in a beaker (?). Agitate and cool in a stream of

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water (?). Note, also, the effect of rubbing the inside of the vessel with a glass rod. Describe the product [Note 39, p. 101]. Filter, and wash the precipitate with a little alcohol.

c. Dissolve a few particles of the precipitate from *b* in a drop or two of warm water and test with litmus (?). Remembering that tartaric acid is a dibasic acid ($H_2C_4H_4O_6$), what sort of salt must the product be?

To a few particles of the precipitate add dilute hydrochloric acid (?).

To a part of the precipitate add drop by drop potassium hydroxide solution (shake between drops) (?). To the resulting solution add concentrated hydrochloric acid a drop at a time. Stir vigorously with a glass rod, and cool in running water between drops (?). Finally, try the effect of excess of the acid (?).

Heat the rest of the precipitate strongly in a porcelain crucible (?). Extract with hot water, filter, and add any acid to the filtrate (?). The ignition of all potassium or sodium salts of organic acids gives the same result.

d. Take 2–3 c.c. potassium chloride solution, and, in another test-tube, dilute a few drops of it with 10 c.c. of water. Then add some picric acid solution to each portion [Note 39, p. 101] (?). Explain the difference in behavior.

What substance is shown to be present in a solution when we get the tests in *b* and *d*?

130. Ammonium Salts.

a. What is a common effect of heating ammonium salts (**92** *e*)? Heat 1 g. of ammonium phosphate in a hard glass test-tube (?). Dissolve the residue in water and test with litmus paper (?). Is simple heating a test for an ammonium salt? Do all salts of ammonium give ammonia when heated (**90** *a*; **98** *a*)? Observe the odors of all the salts of ammonium (solids and solutions) upon the side-shelf (?), and explain.

b. Do ammonium salts impart color to the flame?

c. Take a solution of any ammonium salt and divide it into three portions. To one add excess of tartaric acid solution, and shake (?). To the second add picric acid solution (?). Compare these results with **129** *b* and *d*. To the third add sodium hydroxide solution and note the odor (?). How should you distinguish ammonium-ion from any other ionic substance?

d. Test ammonium chloride solution with litmus (?). Do you infer that ammonium hydroxide is a very inactive base [R 535, 565]?

131. Sodium Carbonate by Solvay Process. Take 75 c.c. of ammonium hydroxide, dilute with 25 c.c. of water, and dissolve

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in it 25 g. of powdered ammonium carbonate by shaking (ammonium hydroxide solution is used instead of water in order to secure ultimately a higher concentration of ammonium-ion than could be obtained with the carbonate alone, the solubility of this salt being too small). Then saturate the solution completely with sodium chloride by prolonged agitation with finely powdered salt in a corked bottle. If crude salt is employed, it should be washed with water before use. Decant the clear liquid into another bottle, fitted with cork and two tubes, one of which reaches to the bottom. If, because of delay, a dense precipitate has appeared, proceed without decanting. Through the latter tube, pass in carbon dioxide from the laboratory supply, or from a Kipp's apparatus, until the solution is saturated. This operation may occupy an hour or more. During the absorption of the carbon dioxide, the exit tube should be closed to prevent waste of the gas. Close the tubes with caps of rubber tubing plugged with glass rods and set aside over night (?). Filter off the deposit, and dry by pressing between filter papers.

Dissolve in water a little of the solid, which must have ceased to smell of ammonia (why?), and test the reaction of the solution with litmus (?). If the solution is not acid, explain why it is not so.

To part of the solid add any dilute mineral acid (?).

Heat the rest in a test-tube clamped so that the mouth is inclined slightly downward, and ascertain what gases are evolved. When gas ceases to be given off, dissolve the cold residue in a very little water, test the reaction of the solution with litmus paper (?), and set it aside to crystallize in an open dish (?). Explain the reaction with litmus (?). Dry the crystals, and ascertain the effects upon them of (a) addition of an acid (?), and (b) of exposure on a watch-glass (?).

Compare the solubilities of the carbonate (Appendix IV) and bicarbonate of sodium [R 544], and explain why the bicarbonate is made first and then the carbonate from it.

132. Purification of Sodium Chloride. Prepare about 150 c.c. of a cold saturated solution of common salt by grinding the salt for some time in a mortar with the water. If crude salt is used, it must first be washed with water. Place the solution in a beaker, and pass hydrogen chloride into the solution. Prepare this gas by placing a handful of common salt in a generating-flask (Fig. 11, p. 29), covering it with concentrated hydrochloric acid, and allowing concentrated sulphuric acid to fall into it from a dropping-funnel. The hydrochloric acid prevents frothing and steadies the stream of gas (why?).

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Deliver the gas into the solution through a thistle-tube with the mouth downward (?). When considerable precipitation has occurred, filter by putting a clean silver coin with milled edges in a funnel, pouring the liquid and crystals upon it, and pressing with a spatula.

Why is the thistle-tube preferable to ordinary tubing?

133. Reactions of Sodium Salts. Take some salt of sodium and try the flame test, and examine the flame with the spectroscope as in **129** *a*. Take a solution of some salt of sodium, and add to one portion picric acid solution (?), and to the other tartaric acid solution (?). Compare all the results with those obtained in **129** and **130** *b* and *c*. How could you distinguish sodium, potassium, and ammonium salts from one another? How could you demonstrate positively the presence both of a potassium and of an ammonium salt in a mixture of the two (a) with and (b) without the aid of the flame test or spectroscope?

Which salts of potassium, ammonium, and sodium are least soluble?

134. Ionic Equilibrium and the Ion-Product Constant.

a. Dilute a few drops of methyl orange solution [R 355] with much distilled water. Add a few drops of an acid (?) and then excess of a base (?). What colors does this indicator show in neutral, acid, and alkaline solution, respectively? What ionic substance is present in the acid, and absent from the other solutions?

Take three portions of distilled water and add to each a little methyl orange solution. To the first two add a little acetic acid (?), to the third a drop of hydrochloric acid (?). To the first add some solid sodium chloride, and shake (?). To the second add some solid sodium acetate, and shake (?). What ionic substance has disappeared? Explain the difference in behavior [R 578]. To the third add solid sodium chloride, and shake (?). Explain the absence of effect.

In what way did **63** *b* illustrate the same principle?

b. Take three portions of a saturated solution of potassium chlorate in as many test-tubes. (If there is any deposit in the bottles, this and the following solutions must be shaken before use to insure saturation.) To the first add saturated sodium chloride solution (?), to the second saturated potassium chloride solution (?), to the third saturated sodium chlorate solution (?). Allow them to stand for a minute or two before drawing any conclusion. Explain [R 581]. The experiments will fail if all the solutions are not saturated.

c. Explain why, in **132**, the salt is precipitated. If the crude salt had contained other salts, which of them would have been

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affected by the introduction of hydrogen chloride, and which not? Specifically, would sodium sulphate or magnesium chloride have been affected, and how? If either of these would be affected and had been present, under what circumstances might it have entered into the precipitate (Appendix IV)? Within what limits, then, does the process give a means of purification?

d. To 1–2 c.c. of concentrated hydrochloric acid add concentrated sulphuric acid drop by drop (?). Explain.

Unknowns (**140**) may be introduced at this point.

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CHAPTER XIX.

METALLIC ELEMENTS OF THE ALKALINE EARTHS.

135. Calcium Oxide. Ignite [Blast-lamp] 2–3 g. of broken marble for 15 minutes in an open crucible placed upon the clay triangle (?). Stir occasionally with the platinum wire. When cool, add a little water (?). Test the reaction of the liquid towards litmus (?). Has water any effect upon marble? Now, add some dilute hydrochloric acid (?). Compare this with the action of the acid upon marble (**109** *b*).

How may the decomposition of the marble be arrested (?) and reversed (?) without altering the temperature? What conditions permitted complete decomposition to take place here?

136. Calcium Hydroxide. Slake a piece of calcium oxide and shake the product with half a liter of distilled water; let the solution settle, or filter rapidly, and use the clear liquid.

a. Blow air from the lungs by means of a tube through a part of the lime-water (?). How could you determine the proportion of carbon dioxide in a sample of air?

b. Dilute the remainder of the lime-water with an equal volume of distilled water, and pass a stream of carbon dioxide from the laboratory supply, or from a Kipp's apparatus, persistently through the solution (?). Boil a part of the resulting clear liquid (?). Explain. Describe all precipitates [Note 39, p. 101], both here and in all succeeding experiments. Why does the second precipitate appear to differ in quantity from the first? What is "temporary hardness" in water [R 594]?

137. Reactions of Calcium Salts. Diluted calcium chloride solution [Note 40, below] may be used for *b*, *c*, *d*, and *f*.

a. Try the flame test and examine with the spectroscope (see that the platinum wire is clean. Note 41, below). Make a sketch of the spectrum showing the positions of the lines with reference to the sodium and potassium lines.

b. To a part of the solution containing calcium-ion add ammonium oxalate solution in excess (?). Filter off the precipitate and divide it into two parts. Place each part in a test-tube, and treat one with dilute hydrochloric acid (?) and the other with diluted acetic acid (?). Explain this difference in behavior towards hydrogen-ion [R 598]. Why was ammonium oxalate used in preference to oxalic acid?

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c. To the second portion of the solution containing calcium-ion add ammonium carbonate solution (?). Warm, if necessary. Filter, divide the precipitate and treat parts of it with hydrochloric acid (?) and diluted acetic acid (?) respectively. Explain the result. Explain also the difference in behavior of the oxalate and the carbonate of calcium towards acetic acid, taking account both of the solubilities of these salts, and of the fundamental difference in behavior between oxalic and carbonic acids.

d. To the third portion of the solution add excess of dilute sulphuric acid (?). Filter and divide the clear (if not, filter again) filtrate into three parts (reserve one for *e*). To one small part add an equal volume of alcohol (formation of all precipitates, if long delayed, may be hastened by vigorous stirring) (?).

Neutralize (test?) the second portion with ammonium hydroxide (why?), add ammonium oxalate solution (?), and explain. Is the sulphate or the oxalate of calcium more soluble? Confirm your inference by giving the solubilities (Appendix IV).

e. What is "permanent hardness" in water [R 595]? Boil the third portion of the filtrate from *d* (?). Compare the result with that in **136** *b*. Add now a little sodium carbonate solution (?). Is the carbonate or the sulphate of calcium more soluble? What are their actual solubilities? How may permanent hardness be removed? What is one objection to the presence of hardness in a domestic water supply (**119** *b*, last par.)?

f. To the fourth portion of the solution containing calcium-ion add some dilute hydrochloric acid, mix, and then add ammonium oxalate solution (?). Explain [R 601]. If any precipitate appears, add more hydrochloric acid. Now add a large amount of sodium acetate solution (?). What is the precipitate (calcium acetate is soluble), and why is it formed [R 601, 650]?

Note 40. — In this and all following paragraphs headed "reactions," where "diluted" solutions are spoken of, the solutions on the side-shelf must be diluted with 3–4 volumes of distilled water to secure good results.

Note 41. — After use, the platinum wire must be cleaned. Form upon it a borax bead, and cause the molten bead to traverse the wire from end to end several times. Throw off the bead. Heat the wire persistently in the Bunsen flame, dipping it from time to time in hydrochloric acid (why?), until the wire no longer colors the flame. If much corroded, the wire may be boiled in nitric acid before being heated.

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138. Reactions of Strontium Salts. Use diluted [Note 40] strontium chloride solution for *b, c,* and *d.*

a. Same as **137** *a.*

b. Add ammonium carbonate solution (?).

c. Add dilute sulphuric acid (?).

d. Add a clear solution of calcium sulphate (made by shaking a little of the pulverized salt with distilled water and filtering until clear) (?). The precipitate may come slowly. Explain.

139. Reactions of Barium Salts. Use diluted [Note 40] barium chloride solution for *b, c,* and *d.*

a, b, c. Same as **138** *a, b, c.*

d. Add a clear solution of strontium sulphate (made by shaking the salt with distilled water and filtering) (?). Explain. Compare with **138** *d,* and arrange the sulphates of these three metals in the order of solubility. Give two methods of distinguishing the compounds of the elements in this family. Examine the table of solubilities (Appendix IV) and suggest another way of distinguishing the three members, and one way of distinguishing calcium-ion and barium-ion, respectively, from the other two. How could you tell a solution containing the ions of a member of this family from one containing those of the members of the previous family?

140. Identification of Unknown Substances. Take three dry test-tubes, apply to the instructor for three "unknown" substances, and ascertain by the use of any experiments you can devise what each is.

a. Study: (1) Physical appearance (?).

(2) Odor (?).

(3) Solubility in water and reaction of the solution toward litmus (?). Use this aqueous solution, and employ the reactions of the metallic ions just studied, for the purpose of recognizing the positive radical. If the substance is insoluble in water, try dilute hydrochloric acid.

(4) Effect of heating in a dry test-tube (?). Observe closely the behavior of the substance, and try to identify the vapors or gases given off. Preserve the residue, as, after the next experiment, examination of this may be necessary.

Before trying this experiment, make a list of all the negative radicals known to you, and place opposite to each the gases, if any, which salts containing that radical, when heated, might be expected to give off. Consider also the means of recognizing these gases, if formed.

(5) Heating with a drop or two of concentrated sulphuric acid (?).

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Before trying this experiment, add to the above list the reactions of sulphuric acid with salts containing each of the negative radicals. Consider also the means of recognizing such of the possible products as are volatile.

(6) Heating the residue from (4) with concentrated sulphuric acid, or such other confirmatory experiments with this residue as the results of (4) and (5) suggest (?).

(7) Other experiments suggested by the results of (1)–(6).

b. Write out the experiments and reasoning carefully in your note-book, and make sure that they prove the substance to be the one you finally decide that it is, and exclude the possibility of its being any other. Report the result to the instructor.

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CHAPTER XX.

COPPER AND SILVER.

141. Cuprous Chloride.

a. Dissolve about 2 g. of cupric chloride in 15 c.c. of water in a small flask. Add 2–3 c.c. of pure, concentrated hydrochloric acid and about 5 g. of copper nails, and boil [Hood] until the green tint is no longer perceptible in the dirty yellowish-brown color of the product. If a few drops added to a test-tube full of water confer a blue tinge upon the water, the action is still incomplete. What ion confers the blue tinge? What change do the cupric ions undergo? Is the change an oxidation or a reduction of cupric chloride?

b. To a small part of the solution, when cold, add excess of sodium hydroxide solution (?). Why is so much of this required? Preserve the mixture in a corked test-tube for use in **143**.

c. Pour the rest of the solution from *a* into a large amount of water in a beaker (?). Expose some of the product, while covered with water, to the sunlight (?).

d. To the rest of the product from *c* add concentrated hydrochloric acid, and shake (?). What is the complex negative ion here formed [R 621]? Does it give a greater or a less concentration of cuprous-ion than does the insoluble cuprous chloride? Upon this basis explain the process of solution here observed. Pour a little of the solution into much water (?).

e. To the rest of the solution made in *d* add a little concentrated nitric acid (?). What ionic substance is shown by its color to be present? Pour this solution into much water (?). Consider each ionic substance originally present in the solution, and explain how it is affected by the nitric acid.

Define this form of oxidation, and the form of reduction in *a*, in terms of the hypothesis of ions.

142. Cupric Hydroxide.

a. To 1–2 c.c. of diluted cupric sulphate solution add excess of sodium hydroxide solution (?). Take one-third of this mixture and boil it (?).

b. Boil 1 g. of sugar dissolved in water (or diluted glucose syrup) with a few drops of dilute sulphuric acid for several minutes (?). This gives glucose and levulose [R 500]. Add

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this glucose solution to another portion of the mixture from *a*, warm gently (?), and note all changes.

c. To the remainder of the mixture from *a* add ammonium hydroxide, and shake (?). What complex ion possesses this blue color [R 623, 625]? Does this ion give a greater or a less concentration of cupric-ion than does the insoluble hydroxide? Upon this basis explain the process of solution here observed.

143. Cuprous Oxide. Divide the mixture from **141** *b*, containing a precipitate of hydrated cuprous oxide, into three parts.

a. Shake one persistently with air in a bottle, admitting fresh air from time to time (?).

b. Boil the second portion (?).

c. To the third portion add ammonium hydroxide (?). What is the color of the mixture? What complex ion is formed [R 622]? Why is cuprous oxide dissolved by ammonium hydroxide solution?

Shake this solution with air. What ion is formed? Is the action more or less rapid than in *a*, and why?

144. Cuprous Iodide. Dilute a few drops of cupric sulphate solution and add potassium iodide solution (?). Filter. Wash the precipitate [Note 38, p. 85] (?). Add part of the filtrate to some starch emulsion (?). Shake the rest with some chloroform (?). Read the footnote to p. 11.

145. Reactions of Cupric Salts. Use diluted cupric sulphate solution. What is the color of cupric sulphate itself? To what is the color of the solution due?

a. Test the reaction of the solution with litmus paper (?) and explain [R 536, 344]. Is copper an active metallic element?

b. Lead hydrogen sulphide through another portion (?). Is this action reversible, theoretically? Add dilute sulphuric acid (?). Do dilute acids act upon any sulphides (**74** *g*)? Why not upon this one [R 600]?

c. To another portion add potassium ferrocyanide solution [R 536] (?).

d. Note here the interaction (**68** *a*) of zinc with cupric-ion (?).

e. Make a borax bead and heat with it a minute particle of cupric oxide in the oxidizing (?) and in the reducing (?) flame, as in **3** *e*. The latter requires patience. If cupric sulphate had been used here, what reaction would have taken place [R 390]?

f. Prepare a match (or splinter of wood) as in **86**. Place on the end a moistened mixture of any copper salt with anhydrous sodium carbonate and heat in the reducing region of a small Bunsen flame. Break up the charred stick gently in water in

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a mortar, wash away the lighter particles, and examine the residue (?).

146. Ammonio-cupric Compounds. To a diluted solution of cupric sulphate add ammonium hydroxide (?), first a drop or two (?), then in excess (?). Of what ion does the copper now form a part? Do other compounds of copper yield the same ion (**142** *c*)? Which action of all those in **145** and **146** should you hold to give the most delicate test for cupric-ion?

Try with the blue solution the tests in **145** *b*, *c*, and *d* (?). Are the concentrations of cupric-ion given by cupric sulphide (?), cupric ferrocyanide (?), cupric sulphate (?), and cupric hydroxide (?), larger or smaller than the concentration of free cupric-ion given by ammonio-cupric-ion? Which of these compounds would be dissolved by ammonium hydroxide solution, and which not?

147. Cuprocyanides. To a diluted solution of cupric sulphate add potassium cyanide solution [CARE! POISON], first a drop or two (?), then in excess (?). Does the solution show the color of cupric-ion? In what form of combination is the copper [R 624]? Divide the solution into three parts and try the tests for cupric-ion given in **145** *b* and *d* (?). Would cupric sulphide dissolve in potassium cyanide solution? Explain your answer. To the third portion add ammonium hydroxide (?). Do cupric sulphide (?) and ammonio-cupric-ion (?) give larger or smaller concentrations of free copper ions than does the cuprocyanide? Would potassium cuprocyanide give the bead test (**145** *e*) or the match test (**145** *f*)?

148. Double Salts (Potassium-Cupric Sulphate).

a. Saturate water at 70° with 5 g. of finely powdered potassium sulphate (about 25 c.c. will be required). Calculate the weight of crystallized cupric sulphate which must be taken to get an equimolecular proportion, and dissolve it in its own weight of hot water. Mix the two solutions, taking care not to allow any undissolved fragments of either salt to get into the mixture, and set the result aside to crystallize (?). Examine the form of the crystals and compare with those of blue vitriol (?). Dissolve a part of the crystals in water and use portions of the solution for *b*.

b. With the solution try tests in **145** *b*, *c*, and *d* (?). Is cupric-ion present? To another portion add ammonium hydroxide (?).

How do double salts differ (a) from complex compounds like potassium cuprocyanide and ammonio-cupric sulphate and (b) from simple salts like cupric sulphate?

149. Equivalent of Copper [Quant.]. Take a small rod of pure zinc, smooth the ends with a file, and weigh carefully.

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Place in a beaker an exactly known weight of crystallized cupric sulphate (about 2 g.), and dissolve in distilled water. Put the zinc in this solution, and allow them to remain in contact until the latter is completely decolorized. Remove the zinc, free it carefully from the brown deposit (?), and dry and weigh it. What weight of zinc has gone into solution?

To avoid weighing the precipitate of copper, which it would be difficult to do exactly, calculate from the formula what quantity of copper was contained in the amount of blue vitriol taken (?). Calculate from your data the weight of copper displaced by the equivalent weight of zinc found in **35** *b* or **36** *a*, or, if zinc was not then employed, assume the latter to be 32.7. This weight of copper will be the equivalent (that of oxygen being 8). Look up the specific heat of copper (Appendix III), and use this and the equivalent observed to find the atomic weight (?).

What other atomic weights could be measured on this plan?

150. Reactions of Silver Salts.

a. Take 1–2 c.c. of silver nitrate solution. Test its reaction towards litmus [R 536] (?). Is silver more or less active as a metallic element than copper?

Add dilute hydrochloric acid until no further precipitation occurs (?). Filter, wash the precipitate with water, and place a small part of it in the sunlight (?).

What effect does the skin have on silver nitrate?

b. To a small part of the precipitate add ammonium hydroxide (?). What complex ion is formed ? Now add dilute nitric acid in excess (?). Formulate the action of this acid.

c. To another small part add sodium thiosulphate solution (?). Pass hydrogen sulphide (see *f*) through the solution (?). Explain both actions.

d. Place the rest of the precipitate in a porcelain crucible; put on it a piece of granulated zinc, and fill up with dilute sulphuric acid. Stir from time to time (?). After an hour or two pour off the acid, take out any unchanged zinc, wash the precipitate with water by decantation, add ammonium hydroxide, and filter. Find out whether any silver chloride had remained unchanged and so passed into the filtrate (**150** *b*) (?). When the filter paper is dry, place the dark powder in a hollow on a stick of charcoal and melt it with the flame of the blast-lamp directed downward upon it (?).

e. Dilute a few drops of silver nitrate solution and divide into two parts. To one add potassium bromide solution (?), and to the other potassium iodide solution (?). Add to each some ammonium hydroxide (?). Compare the rates of action

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with that on silver chloride (?). Arrange the three salts and ammonio-argentic-ion in the order of decreasing ability to give argentic-ion (?). Relate this order to that of solubility (Appendix IV).

f. Dilute 2–3 drops of silver nitrate solution and lead in hydrogen sulphide (?). Is this action reversible, theoretically? Divide the product into two parts, and to one add dilute nitric acid (?).

To the other part add potassium cyanide solution [CAUTION! POISON] (?). What is formed? Could silver chloride be precipitated from this solution (**54** *b*)? Explain.

g. To 1 c.c. of silver nitrate solution add a few drops of potassium dichromate solution (?). Test the solutions before (?) and after mixing (?) with Congo red paper [R 355]. (If the color of the dichromate obscures that of the Congo red, wash the test-paper with distilled water.) What product does this show? Make the equation accordingly.

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CHAPTER XXI.

MAGNESIUM, ZINC, CADMIUM, MERCURY.

151. Magnesium. Mix thoroughly in a mortar equal bulks of magnesium powder and powdered calcium carbonate. Put the mixture in a test-tube (it should fill about half an inch of the tube), fix the tube in a clamp on the stand, and heat the top layer in the Bunsen flame until the reaction begins. Be careful to keep the tube directed away from the face during the heating. Allow the test-tube to cool, add a little water, and then, slowly, an excess of concentrated hydrochloric acid (?). (If the tube has been broken, place the contents with the acid in a beaker.) What effect will the acid have upon any excess of either of the ingredients? The acid will also dissolve the oxides of magnesium and calcium formed by the action. When all action has ceased, filter and wash the black residue (?) with water. After drying this on the radiator or water bath, prove that it is carbon. This may be done by placing some of it in a dry test-tube, adding a pinch of potassium chlorate, heating in the Bunsen flame, and pouring the gas when it has cooled (close the tube with the thumb while waiting for this) into a test-tube containing 2 c.c. of lime-water, and shaking (?).

What is the reducing agent in this action?

Examine the test-tube (?) and explain [R 518].

152. Properties of Magnesium Compounds.

a. Try whether magnesium chloride dissolves completely in water (?). Test the solution with litmus (?).

Heat some of the crystals strongly in a dry test-tube (?). Test the reaction towards litmus paper of the water which condenses in the tube (?), and then remove the liquid from the sides of the tube with a piece of filter paper. Does the residue dissolve in water? Explain.

b. To some diluted magnesium sulphate solution add ammonium hydroxide (?). Explain the result in terms of the ion-product constant [R 587] (?). Now mix with some ammonium hydroxide several times its volume of ammonium chloride solution (what effect will this have on the ionization of ammonium hydroxide? Would ammonium sulphate answer as well?), and then add the mixture to a new portion of magnesium sulphate solution (?). Explain in terms of the ion-product constant.

To this combination of three solutions add sodium phosphate

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solution (see **106** *c*) (?). Explain the purpose of each ingredient.

c. To a fresh portion of the diluted magnesium sulphate solution add ammonium carbonate solution, and warm (?). Repeat, adding excess of ammonium chloride solution to the magnesium sulphate solution before using the carbonate (?).

Calcium-ion (**137** *c*), strontium-ion (**138** *b*), and barium-ion (**139** *b*) were also precipitated by ammonium carbonate. Repeat these experiments with them, adding first excess of ammonium chloride solution (?). If you had a salt of magnesium mixed with a salt of one of those other metals, how should you proceed so as to precipitate a compound of the alkaline earth metal first and one of magnesium afterwards?

Add two drops of hydrochloric acid (why?) to about 250 c.c. of the city water, evaporate to small bulk, and test it for calcium-ion and magnesium-ion.

d. Pass hydrogen sulphide through magnesium sulphate solution (?).

153. Reactions of Zinc Salts. Use diluted zinc sulphate solution.

a. Test the solution with litmus paper (?). Explain.

b. To a part of it add sodium carbonate solution (?), at first a little and then in excess. Note the gas evolved (?). Why is the gas slow in appearing? Relate this result to that in *a* (?). Bring the contents of the tube to the boiling-point, filter, and wash the precipitate with water. To a portion of the precipitate add an acid (?). Account for the evolution of gas during the precipitation. Dry the rest of the precipitate for *c*.

c. Heat the dried, basic zinc carbonate from *b* in a porcelain crucible to redness for a few minutes. Remove a small portion of the product and try the action of an acid upon it (?). If it effervesces, ignite for a longer time. What is the color of the product when hot, and when cold? Reserve for *d*.

d. Moisten the residue from *c* with a few drops of a cobalt chloride solution and heat again (?).

e. To another part of the zinc sulphate solution add a very little sodium hydroxide solution, and shake (?). Filter, suspend the precipitate in water, and divide into three parts. To one add an excess of sodium hydroxide solution (?). Does this show zinc hydroxide to be basic, or acidic? To the second portion add dilute hydrochloric acid (?). What sort of hydroxide does it now seem to be? Explain [R 648].

To the third portion add ammonium hydroxide (?). What complex ion is formed [R 648] ?

f. To a third portion of zinc sulphate solution add ammo-

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nium sulphide solution (?). Filter, and preserve the precipitate for *g*.

g. Roll up a small part of the filter paper from *f* into a ball, and coil the platinum wire tightly round it. Roast the whole in the Bunsen flame (?). Moisten the ash with cobalt chloride solution and heat again (?).

154. Relative Activity of Several Acids. In clean test-tubes place equal volumes of (1) zinc chloride, (2) zinc sulphate, and (3) zinc acetate solutions. Compare their reactions towards litmus and towards Congo red paper [R 356] (?). Into each pass hydrogen sulphide to saturation (test? Note 36, p. 67) (?). Are actions like this reversible, theoretically? The reverse action consists in the action of what acid upon what insoluble salt in each case? Will it be equal with different acids [R 599]? If not, the most active acid will have kept the most zinc in solution and the least active the least. To ascertain how much zinc remains in each solution, filter the mixtures separately, and, after testing with Congo red paper (?), add ammonium hydroxide to each (?). The precipitates are zinc sulphide (why?), Compare the amounts (?). Infer the relative activities of the acids (?).

Confirm the conclusion, roughly, by putting some of the precipitate into each of three test-tubes, treating directly with dilute hydrochloric, sulphuric, and acetic acids, of equivalent concentrations, and comparing the rates of action (?).

Why was ammonium sulphide used in **153** *f* ?

155. Ionic Equilibrium. Take a larger amount of zinc sulphate solution, and add sulphuric acid to it cautiously until a sample just ceases to give any precipitate with hydrogen sulphide. Explain. Now add much powdered, anhydrous sodium sulphate, stir until it has dissolved, and test a part with hydrogen sulphide again (?). What effect must the great addition of sulphate-ion have upon the hydrogen-ion introduced by the sulphuric acid? Why is zinc sulphide now precipitated?

156. Reactions of Cadmium Salts. Use diluted cadmium sulphate solution.

a. Same as **153** *e*. Answer the same questions.

b. Saturate with hydrogen sulphide (?). Is the action easily reversible? Add dilute hydrochloric acid (?).

By what reactions could you distinguish between salts of magnesium, zinc, and cadmium?

157. Unknown Substances. Apply to the instructor for three unknown substances. To identify the anions, follow the outline of work in **140**. To identify the cations, employ

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the scheme commonly used in analysis [R 660]. Present to the instructor a logical and coherent, written report.

158. Mercurous Nitrate. Place about 10 g. of mercury with 15 c.c. of diluted (1 : 1) nitric acid in a small beaker, and let the action go on for an hour. Stirring will cause crystallization. Dissolve the crystals in water to which a few drops of nitric acid have been added (why?). Use this solution in **160**.

159. Mercuric Nitrate. Boil some mercury or mercurous nitrate with excess of concentrated nitric acid. Evaporate the solution on a water bath, moisten with nitric acid, and dry.

160. Reactions of Salts of Mercury. Use diluted portions of mercurous nitrate solution and of a diluted solution of any mercuric salt, and add to each the following reagents. Compare the results in each case.

a. Litmus paper (?). Explain.

b. Dilute hydrochloric acid (?). Treat the precipitate, if there is any, with ammonium hydroxide [R 659] (?).

c. Sodium hydroxide solution [R 656] (?).

d. Ammonium hydroxide [R 659] (?).

e. Hydrogen sulphide to saturation [R 657] (?).

f. Potassium iodide solution (shake) until there is no further change (?). What complex ion is formed? Try an experiment to show that mercuric sulphide gives an even smaller concentration of mercuric-ion than does this complex ion (?).

g. Stannous chloride till there is no further change [R 655] (?).

h. A clean copper nail (?). Determine whether any copper goes into solution (?). Explain (Appendix VII).

i. Heat a little of a salt of mercury in a dry test-tube (?).

j. How could you distinguish a solution of a mercurous and of a mercuric salt, respectively, from salts of silver, copper, magnesium, zinc, and cadmium?

Do magnesium, zinc, cadmium, and mercury exhibit the properties of typical metallic elements [R 533]? Explain.

161. Concentration Cell. Suspend a rod of tin about 60 mm. long by a thread from one end, and hang it near the bottom of the graduated cylinder. Pour in through the dropping-funnel, which must reach the bottom of the cylinder, first highly diluted, dilute hydrochloric acid (1 : 6 Aq.) and then diluted (1 : 1) stannous chloride solution. Perform the operation with care, in such a way that the solutions do not mix, the dilute acid being finally uppermost, and that the surface at which they meet is near the middle of the rod of tin. If the second solution is permitted to carry air bubbles with it, mixing will inevitably occur. Place the arrangement where it will not be disturbed, and examine from time to time (?). Explain [R 673].

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CHAPTER XXII.

ALUMINIUM, TIN, LEAD.

162. Aluminium.

a. Record here the action of aluminium on hydrochloric acid (**16** *a*) and its degree of intensity (?). Try the action of the metal on dilute sulphuric (?) and dilute nitric acids (?). Compare and explain.

b. Heat some aluminium turnings with sodium hydroxide solution for some minutes (?). To ascertain whether anything has gone into solution, neutralize one-half of the liquid carefully with dilute hydrochloric acid (?). Test the precipitate by **163** *f* (?).

c. To the rest of the liquid from *b* add calcium chloride solution (?). To what group of minerals do compounds allied to this belong [R 685] ?

163. Reactions of Aluminium Salts. Use portions of diluted aluminium sulphate solution.

a. Test the solution with litmus paper (?). Explain.

b. Add ammonium sulphide solution (?). Filter off the precipitate, wash it until odorless (why?), and ascertain whether it is a sulphide or not (?). Preserve a part of it for *f*.

c. Add sodium carbonate solution (?). Filter off the precipitate, wash it until free from sodium carbonate (why?), and ascertain whether it is a carbonate or not (?).

d. Add a little sodium hydroxide solution (?). Proceed as in **153** *e*, and answer the same questions (?). Explain the difference in behavior observed (?).

e. To a small portion add sufficient sodium hydroxide solution to redissolve the precipitate. Then add excess of ammonium chloride solution, and boil (?). Explain.

f. Proceed as in **153** *g* with a small part of the filter paper from *b* (?) (or use the method in **153** *d*).

164. Alum. Prepare warm, saturated solutions of hydrated aluminium sulphate and ammonium sulphate in approximately equimolecular proportions (calculate amounts required), mix them, and set aside (?). Obtain some large crystals by hanging a thread in the solution. Note the form and taste of the crystals (?).

Dissolve one or two of the crystals, and ascertain by experiments selected from **163** whether the solution contains alu-

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minium-ion (?). Infer whether this is a double salt, or a salt giving a complex ion.

165. Mordanting.

a. To some cochineal solution add any solution containing a salt of aluminium and then ammonium hydroxide (?). Filter. What becomes of the coloring matter?

b. Soak a small piece of cloth in a strong solution of alum (made in **164**), and then transfer it to a beaker containing a boiling solution of cochineal made strongly alkaline with ammonium hydroxide (?). What purpose does the alum serve? What is the object of the ammonium hydroxide? What compounds of aluminium would act as mordants without the addition of a base (?), and how do they so act [R 689]?

166. Tin. Place some tin (gran.) in a test-tube with diluted nitric acid (1 acid: 10 Aq) and set aside. After **168**, examine portions of the solution. Determine whether it contains a salt of ammonium (?), and explain. Determine whether it contains stannic-ion or stannous-ion (?). How does tin behave with concentrated nitric acid (**97** *e*)? Explain the difference.

167. Halides of Tin.

a. Stannous halide. Heat about 1 g. of tin with pure, concentrated hydrochloric acid (see **16** *a*) (?). Let the action go on until the acid is nearly exhausted. Use the solution in *b*, and in **168**. Proceed with later experiments until it is ready.

b. Stannic halide [Hood]. To one-half of the solution from *a* add bromine-water until the color ceases to be destroyed, and drive off the excess of bromine by warming (?). Use this liquid in **168**.

168. Reactions of Stannous and Stannic Salts. In *a*, *b*, and *c* use a portion of each of the solutions from **167**, after dilution, with each reagent. Compare the two results in each case.

a. Saturate (test?) each portion with hydrogen sulphide (?). To part of each product add dilute hydrochloric acid, to learn whether the action is easily reversible (?). Filter the remainder of each product, and treat the precipitates, separately, with warm yellow ammonium sulphide solution [R 697] (?). To the resulting liquids add dilute hydrochloric acid (?). Explain why both give the same product (?). What is the gas evolved?

b. Add mercuric chloride solution, at first a little and then in excess, first to the stannic (?) and then to the stannous solution (?). When the changes (two) in the latter are complete, boil, let the precipitate settle, filter the clear part of the liquid, and determine whether the tin in the filtrate is now stannous or stannic by adding a drop or two of bromine-water (see **167** *b*).

c. Add to each portion a little sodium hydroxide solution (?).

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Proceed as in **156** *e* and answer the same questions (?). Explain the difference, if any, in behavior observed. What other hydroxide resembles those of tin and zinc?

d. Boil a small portion of the stannic solution with tin (gran.) for several minutes. Now add mercuric chloride solution (?) and compare with the results in *b* (?). Account for the change in the stannic-ion (?). What kind of chemical change was this?

169. Apply to the instructor for two unknown substances. Identify them, and report the result, as directed in **140** and **157.**

170. Lead.

a. Dissolve 1 g. of lead acetate in 20 c.c. of water, place in it several pieces of granulated zinc, and set aside for an hour or two. After **171** devise a way of precipitating any remaining lead-ion and showing the presence of zinc-ion in the solution.

b. Wash some of the lead from *a* with distilled water, and see whether it is possible to get washings which show no reaction with hydrogen sulphide (?). Account for what you observe.

171. Reactions of Lead Salts. Use diluted lead nitrate.

a. Test with litmus paper (?).

b. Saturate (test?) with hvdrogen sulphide (?). Is the action easily reversed?

c. Add dilute hydrochloric acid (?). Filter, dilute the filtrate with 5–10 volumes of water, and saturate with hydrogen sulphide (?). Explain. What other chlorides are "insoluble"?

d. Add sodium hydroxide (?), first a little, then in excess. What other hydroxides resemble this one?

e. Add potassium iodide solution (?). Boil, filter, and examine the filtrate (?). Infer a property of lead iodide (?).

f. Potassium dichromate solution (?). Proceed as in **150** *g* (?).

g. Dilute sulphuric acid (?). What sulphates are insoluble?

172. Lead Dioxide.

a. Warm and agitate 1 g. of minium with 5–6 c.c. of dilute nitric acid until it no longer changes in color (?). Dilute with water, and filter. Reserve the precipitate for *b* and *c*. Show by tests selected from **171** that lead-ion is present in the filtrate. What theory of the nature of red lead is suggested by this action [R 701]?

b. Treat a part of the precipitate from *a* with sodium hydroxide solution (?). Record here the action of hydrochloric acid upon lead dioxide (**29** *a*) and explain it (?).

c. Allow the rest of the precipitate from *a* to dry, place it in an evaporating-dish, and direct upon it a stream of hydrogen sulphide (?). Explain.

173. Do aluminium, tin, and lead exhibit the properties of typical metallic elements [R 533]? Explain.

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CHAPTER XXIII.

ARSENIC, ANTIMONY, BISMUTH.

174. Arsenic.

a. Heat one particle of arsenic in a hard glass test-tube (?).

b. Roast a particle of arsenic on a crucible lid (?). Note the behavior and odor (?).

c. Mix a pinch of pulverized arsenic trioxide with wood charcoal (pulv.). Heat the mixture strongly in a dry test-tube (?). Compare result with *a* (?).

d. Boil 0.5 g. of arsenic (pulv.) with excess of nitric acid (?). Compare with **105** *b*. Use the solution for **177** *e*.

175. Arsenic Trioxide and Arsenious Chloride.

a. Boil 0.5 g. of arsenic trioxide with water (?). Test the solution with litmus (?). Now add sodium hydroxide solution, and boil (?). To what class of oxides does the trioxide appear to belong? Formulate the whole change.

b. Boil 1 g. of the trioxide with 2–3 c.c. of concentrated hydrochloric acid (?). To what class of oxides does it appear now to belong? Formulate this change. Set aside and examine later (?). What are the crystals [R 710]? Is this action reversible? Use the solution for *c* and **178**.

Is arsenic a typical metallic element? Is it a metal at all? Give reasons taken from *a* and *b*.

c. Take a small part of the solution from *b* (setting aside the rest), dilute with water, and saturate with hydrogen sulphide (?). Divide into two parts. With one, try whether the action is easily reversible (?). Filter the other and heat the precipitate with yellow ammonium sulphide solution (?). What other sulphide behaved in this way? Now add dilute hydrochloric acid to the liquid (?). Explain. What is the gas evolved?

176. Arsenites. Use portions of diluted potassium arsenite solution.

a. Add silver nitrate solution (?), then ammonium hydroxide (?).

b. Add cupric sulphate solution [R 712] (?).

c. Test the solution with litmus (?). What substances must be present? Saturate with hydrogen sulphide (?).

177. Arsenic Acid and Arsenates. For *a, b, c,* and *d,* use portions of diluted potassium arsenate solution.

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a. Add **silver nitrate solution** (?). Add **now ammonium hydroxide** (?).

b. Add **magnesia mixture (106 *c*)** (?). Compare with **152** *b* (?).

c. Add to ammonium molybdate solution as in **105** *c* (?).

d. Add 2–3 drops of dilute hydrochloric acid (?) and saturate with hydrogen sulphide (?). Now add excess of concentrated hydrochloric acid and saturate again (?), heating to assist the action. Explain.

e. Neutralize the solution from **174** *d* with ammonium hydroxide, avoiding excess, and use tests selected from *a*, *b*, and *c* (?).

178. Arsine [Hood. Care! Poison]. Arrange a side-neck test-tube (or small flask) with safety and straight delivery tubes and nozzle to generate and burn hydrogen. Place in it a piece of chemically pure zinc, and add pure hydrochloric acid [Side-shelf]. When the air has been displaced (Care. Test?), light the gas and hold a crucible lid in the flame (?). If there is no deposit, add a drop or so of the solution of arsenic trichloride (**175** *b*), observe the appearance of the flame, and obtain a deposit on the crucible lid (?). What kind of chemical change takes place in the flame (see **72** *b*)? Heat the tube, through which the gas passes to the nozzle, with a Bunsen flame (? Marsh's test). When these experiments are completed, fill the test-tube with water to stop the action.

Apply bleaching powder solution (fresh) to the deposit (?).

Can arsine be made according to the general method considered in **115**? What other hydrides behave like arsine when heated?

179. Antimony.

a, *b*. Proceed as in **174** *a* and *b*, using antimony (?).

180. Antimony Trioxide.

a. To obtain the trioxide, heat 2–3 g. of pulverized antimony with concentrated nitric acid in a small flask [Hood] (?). How should you determine whether the product was a nitrate or not? (?). What other metal behaved similarly when treated with nitric acid? Compare with arsenic (**174** *d* and **177** *e*) (?). Dilute, filter, wash well [Note 38, p. 85], and use in *b*, *c*, *d*, and *e*.

b. Boil a small part with water (?). Add sodium hydroxide solution, and boil (?). What kind of oxide is it?

c. Boil a small part with hydrochloric acid (?). What kind of oxide is it?

d. Boil a part with an equal amount of potassium-hydrogen tartrate in 5–6 c.c. of water (?). Filter, and set the filtrate aside (?). What are the crystals?

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e. Boil the rest persistently with 2–3 c.c. of concentrated nitric acid (?). Evaporate [Hood] the clear liquid, and heat the residue a little below a red heat [R 715] (?).

181. Antimony Trichloride and Trisulphide.

a. Treat about 0.5 g. of antimony trichloride with water (?), and test the liquid with litmus paper (?). Add more water, warm, and ascertain whether the action is reversible by adding drop by drop (shake between drops) concentrated hydrochloric acid (?). When the liquid has become clear add a large amount of water (?). What law is illustrated? Finally, add concentrated hydrochloric acid again (?), and use the solution in *b*.

How does this action differ from that of water upon phosphorus trichloride (**107** *b*) and upon arsenic trichloride [R 710]? What is the significance of this difference?

b. Dilute the liquid from *a*, saturate with hydrogen sulphide (?), and proceed as in **175** *c* (?). Answer the same questions.

182. Stibine. Repeat **178,** using antimony trichloride (?).

183. Bismuth. Prepare a match (or splinter of wood) as in **86**, and proceed as in **145** *f*, using any bismuth salt (?). What metals are obtainable in this precise way? Could zinc, mercury, silver, and aluminium be so obtained? Explain.

184. Compounds of Bismuth.

a. Warm about 1 g. of bismuth with 8–10 c.c. of diluted (1 : 1) nitric acid (?). Concentrate to 3 c.c. and set aside [R 718] (?). Compare this result with arsenic (174 *d*) and antimony (**180** *a*), and interpret (?).

b. Proceed as in **181** *a* (first par.), using bismuth nitrate (or the product from *a*) and nitric acid, instead of the salt and acid there employed (?).

c. Take 1–2 c.c. of bismuth nitrate solution, dilute it, and clear up with nitric acid if necessary. Saturate a part with hydrogen sulphide (?), and proceed as in **175** *c* (?). Compare with the sulphides of arsenic and antimony (?).

d. To the remainder of the solution of bismuth nitrate add sodium hydroxide (?), at first a little, and then in excess (?). Compare this hydroxide with the oxides of arsenic (**175** *a*) (?) and of antimony (**180** *b*) (?).

Filter off the precipitate, ignite it in a porcelain crucible, and note the color (?) when hot (?) and when cold (?).

185. Do arsenic, antimony, and bismuth exhibit the properties of typical metallic elements? If not, in what respects do they fail to do so?

186. Apply to the instructor for two unknown substances. Identify them, and report the result, as directed in **140** and **157.** Do not use Marsh's test for arsenic.

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CHAPTER XXIV.

CHROMIUM, MANGANESE.

187. Chromates. Melt 5 g. of potassium carbonate with equal amounts of potassium hydroxide (omit this from the equation) and potassium nitrate (include only oxygen, from this, in the equation) at a low temperature in an iron crucible [Storeroom] and stir in (use the reverse end of a file) 5 g. of powdered chromite. Heat strongly [Blast-lamp] for several minutes (?). When the mass has cooled dissolve it in a little boiling water. Filter, and add dilute nitric acid to the solution until it is acid (?). Note the change in color (?).

188. Dichromates and Chromates. Take some potassium dichromate solution and run into it potassium hydroxide solution from a burette till the change in color is complete. A test-tube trial will show the tint to be reached. Concentrate the solution and allow it to crystallize (?). What kind of salt (neutral, acid, basic, double, or complex) is potassium dichromate essentially? What are the colors of dichromate-ion and of chromate-ion?

189. Chromic Anhydride. Make a cold saturated solution of 5 g. of sodium dichromate, add to it two volumes of concentrated sulphuric acid in a beaker, and cool (?). Filter through a small plug of asbestos, and dry the precipitate by smearing it on a piece of broken bisque plate [Storeroom].

190. Chromic Oxide. Pulverize potassium dichromate (10 g.) thoroughly with one-fifth its weight of sulphur, and heat with the blast-lamp in a porcelain crucible for fifteen minutes. Grind up the resulting mass in a mortar with water, filter, wash the green residue (?), and dry it on a radiator for use in **191**.

Make a borax bead, dissolve a particle of chromic oxide in it, and note the effects of the oxidizing and reducing flames upon it (?). All chromium compounds give the same result. If chromic sulphate had been used, what would have been the nature of the chemical action?

191. Chromic Chloride. Mix the chromic oxide prepared in **190**, with one-third its weight of pulverized wood charcoal, make into a stiff paste with some starch, and mold the mixture into little pellets of the size of peas. Cover these completely with a layer of charcoal powder (why?) in a closed crucible.

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dry them by heating gently with the Bunsen flame, and let them cool before exposing them to the air (why?). Place them in a piece of hard glass tubing. Then connect with a chlorine apparatus, and, when the chlorine gas has reached the pellets and completely displaced the air (why?), heat strongly with a blast-lamp. Conduct any superfluous chlorine into a test-tube filled with sodium hydroxide. Describe the substance which is formed, and try its solubility in water and acids.

192. Chrome-Alum. Dissolve 10 g. potassium dichromate in water, add the amount (calculated) of sulphuric acid necessary to form potassium sulphate and chromium sulphate, warm and add alcohol (7–10 c.c.), a little at a time, until the yellow color has entirely given place to a pure, bright green. The action takes some time to reach completion. Note the odor (?). Set the greater part of the solution aside to evaporate spontaneously. Concentrate the smaller portion on the water bath until crystals appear. Examine the form and color of the crystals from both portions (?). What is the color of their solution in water? What is the color of chromic-ion?

193. Reactions of Chromic Salts. Make a solution of chrome-alum. What are the ions in the solution?

a. Boil a portion for some time [R 730].

b. To another portion add sodium hydroxide solution, at first a little (?), then in excess (?). Boil [R 729].

c. Add ammonium sulphide (?). Filter off the precipitate, wash it until odorless, and determine whether it is a sulphide.

d. Add excess of sodium hydroxide solution and then a large volume of bromine-water, and heat (?). Try another portion, using lead dioxide instead of bromine (?). Infer the nature of the action from the change in color.

194. Reactions of Chromates. For *a, b, c, d,* use diluted potassium chromate solution. What are the ions in the solution?

a. Acidify a part of the solution with dilute sulphuric acid (?). Concentrate and set aside to crystallize (?).

b. Recall the actions of hydrogen sulphide, of sulphurous acid, and of hydrogen peroxide, on such an acid solution (?).

c. Add ammonium sulphide, heat and maintain at the boiling-point, noting two distinct changes (?), then acidify (?).

d. Add lead nitrate and barium chloride solutions to separate portions (?).

e. Repeat *d* with potassium dichromate solution (?). Compare the results and explain.

195. Manganates and Permanganates.

a. Fuse a mixture of 5 g. of potassium hydroxide, 2.5 g. potassium chlorate (include only the oxygen, from this, in the equa-

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tion), and 5 g. finely powdered manganese dioxide, at a red heat, in an iron crucible [Storeroom], stirring with the reverse end of a file, until effervescence ceases (?). Add the last ingredient gradually. Treat the mass with a small amount of cold water, decant the clear liquid away from the precipitate, and use it in *b*, *c*, and *d*. What is the color of manganate-ion?

b. Dilute a part of the clear green solution with a very large amount of water in a beaker (?). If no change should occur, pass carbon dioxide into the diluted solution (?). What is the color of permanganate-ion? How does this substance differ from manganate-ion?

c. Add a few drops of alcohol, and warm (?).

d. To the rest add a boiling solution of oxalic acid (?).

e. Repeat *c* and *d* with potassium permanganate solution, acidified by adding two or three times its volume of dilute sulphuric acid (?).

f. Recall the actions of hydrogen peroxide (**60** *c*), hydrogen sulphide (**73** *f*), and sulphurous acid (**83** *g*) on acidified potassium permanganate solution (?).

196. Reactions of Manganous Salts. Use any manganous salt. What is the color of manganous-ion?

a. Borax bead in the oxidizing (?) and reducing (?) flames.

b. Bead of a mixture of sodium carbonate and sodium nitrate on a platinum wire with any manganese compound (?).

c. To a diluted solution of a manganous salt, add ammonium sulphide (?). Is the product a sulphide?

d. To another portion add sodium hydroxide (?). Divide into two parts. Shake one with air (?). To the other add bromine-water, and warm (?).

197. Apply to the instructor for two unknown substances. Identify them, and report the result, as directed in **140** and **157**.

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CHAPTER XXV.

IRON, COBALT, NICKEL.

198. Iron. Recall the preparation of iron from an oxide (**20**), and the action of the metal on dilute acids (**16** *a*) (?).

199. Reactions of Ferrous and Ferric Salts: I.

a. Borax bead with any compound of iron (use the oxide) in the reducing (?) and oxidizing (?) flames.

b. Recall the action of heat upon ferric nitrate (**35** *a*) and upon ferric sulphate (**82**) (?).

Prepare a dilute solution of ferrous-ammonium sulphate [Note 37, p. 68]. Dilute some ferric chloride solution [Note 40, p. 108]. Use portions of these solutions, and add to each the following reagents. Compare the results in each case.

c. Ammonium hydroxide (?). Shake with air (?).

d. Potassium ferrocyanide solution (?).

e. Potassium ferricyanide solution (?) and add much water.

f. Ammonium thiocyanate solution (?).

g. Ascertain by tests whether the commercial hydrochloric acid contains ferrous-ion or ferric-ion (?). Show that it contains also sulphuric acid (?).

200. Reactions of Ferrous and Ferric Salts: II. Reductions and Oxidations. Use diluted ferrous-ammonium sulphate and diluted ferric chloride solutions.

a. To portions of each solution add ammonium sulphide solution (?). Ascertain in each case whether the action is easily reversible (?). Explain the behavior of the ferric chloride solution [R 756] (?). How could you determine whether the free sulphur was formed before or after the acidification?

b. To portions of each solution add potassium iodide solution (?). To a little starch emulsion add a few drops of the ferric-potassium-iodide mixture (?).

c. Saturate (test?) a portion of the ferrous solution with hydrogen sulphide (?). Explain in terms of the ion-product constant (?). Now add ammonium hydroxide (?). Filter. Wash the precipitate until odorless, and determine whether it is a sulphide or hydroxide (?). Explain in terms of the ion-product constant.

d. Saturate (test?) a portion of the ferric solution with hydrogen sulphide (?). Filter. What is the precipitate (test?)? Examine the clear filtrate, and determine, by means of tests

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from **199** *d, e,* and *f,* whether ferric-ion or ferrous-ion is present (?). Formulate the action of the hydrogen sulphide.

e. Boil a portion of the ferric solution with excess of pulverized iron for several minutes. Filter, and apply to part of the clear filtrate (color?) tests selected from **199** *d, e,* and *f* (?). Formulate the action of the iron. Use the rest of the filtrate in *f*.

f. To 2 c.c. of potassium permanganate solution add a large excess of dilute sulphuric acid (?). Add this mixture drop by drop to the rest of the filtrate from *e* until the pink color is permanent [R 744] (?). Apply to this liquid tests from **199** *d, e,* and *f* (?). Formulate the action in terms of ions alone. Which kinds of ionic chemical change have been illustrated here? How could this action be used for estimating iron?

What other oxidizing agents convert ferrous into ferric salts (see **94** *f*)?

201. Hydrolysis. Dissolve 0.5 g. each of ferric sulphate and ferrous-ammonium sulphate separately in water, and warm very slightly. Observe the tints by looking downward through the solutions at a piece of white paper (?). Test each solution with Congo red paper, compare (?), and interpret the results. Now add some pure sulphuric acid to each and observe the tints again. Explain. What are the colors of ferrous-ion and ferric-ion, respectively? Which of these allotropic forms of the element is more typically metallic?

202. Iron-Ammonium Alum.

a. Weigh 6 g. of ferric sulphate into an evaporating-dish. Weigh out an equimolecular quantity (calculate) of ammonium sulphate. Dissolve the salts separately, each in the minimum amount of boiling water, mix the solutions, and set aside (?). Describe the crystals (?). Collect them upon a filter, wash them free from the mother-liquor, and dry with filter paper.

b. Ascertain (see **199** *c, d, e*) whether iron-alum is a double salt, or a salt of a complex acid (?).

203. Ferrocyanides and Ferricyanides. Use diluted potassium ferrocyanide solution.

a. Add ammonium hydroxide (?) and compare with **199** *c* (?).

b. Add ammonium sulphide solution and compare with **200** *a* (?). Is ferrous-ion present?

c. Add bromine-water (shake) in excess, and boil off the superfluous bromine. To a part of the liquid add ferric chloride solution (see **199** *d* and *e*) (?).

d. To the rest of the liquid from *c* apply the tests in **199** *c* and *f* (?). Is ferric-ion present?

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204. Reactions of Cobalt Salts. For *b* and *c* use diluted cobalt chloride solution.

a. Borax bead in oxidizing (?) and reducing (?) flames.

b. Sodium hydroxide solution, first a little (?), then in excess, and warm (?).

c. Ammonium sulphide solution (?).

205. Reactions of Nickel Salts. For *b* and *c* use diluted nickel sulphate solution.

a, b, c. Same as in **204.**

206. Apply to the instructor for two unknown substances. Identify them, and report the result, as directed in **140** and **157.**

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APPENDIX.

I. Correction of Barometric Readings.

To reduce the reading taken at room temperature (Temp.) to the corresponding height of a column of mercury at 0°, subtract the proper number in the second column (Corr'n) from the actual reading in millimeters. [See Note 31, p. 18.]

Temp.	Corr'n.	Temp.	Corr'n.	Temp.	Corr'n.
12	1.6	17	2.2	23	3.0
13	1.7	18.5	2.4	24.5	3.2
14	1.8	20	2.6	25	3.3
15	2.0	21.5	2.8	26	3.4

II. Tension of Aqueous Vapor in Millimeters.

Temp.	Press.	Temp.	Press.	Temp.	Press.
0°	4.6	16°	13.5	26°	25.1
5	6.5	17	14.4	27	26.5
8	8.0	18	15.4	28	28.1
9	8.6	19	16.3	29	29.8
10	9.2	20	17.4	30	31.5
11	9.8	21	18.5	31	33.4
12	10.5	22	19.7	32	35.4
13	11.2	23	20.9	33	37.4
14	11.9	24	22.2	34	39.6
15	12.7	25	23.6	100	760.0

III. Specific Heats of Metals.

Aluminium	0.214	Iron	0.114	Magnesium	0.250
Copper	0.095	Lead	0.031	Zinc	0.095

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IV. Solubilities of Bases and Salts in Water at 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95 3.9	35.86 5.42	77.79 13.3	0.0_316 0.0_410	0.3 0.013	37.24 1.7	51.09 3.0	73.19 5.4	55.81 5.1	203.9 9.2	1.49 0.05
Br	65.86 4.6	88.76 6.9	168.7 12.6	0.0_41 0.0_66	0.04 0.0_215	103.6 2.9	96.52 3.4	143.3 5.2	103.1 4.6	478.2 9.8	0.598 0.02
I	137.5 6.0	177.9 8.1	161.5 8.5	0.0_635 0.0_71	0.006 0.0_317	201.4 3.8	169.2 3.9	200 4.8	148.2 4.1	419 6.9	0.08 0.0_22
F	92.56 12.4	4.44 1.06	0.27 0.11	195.4 13.5	72.05 3	0.16 0.0_292	0.012 0.001	0.0016 0.0_32	0.0076 0.0_214	0.005 0.0_35	0.07 0.003
NO_3	30.34 2.6	83.97 7.4	71.43 7.3	213.4 8.4	8.91 0.35	8.74 0.33	66.27 2.7	121.8 5.2	74.31 4.0	117.8 4.7	51.66 1.4
ClO_3	6.6 0.52	97.16 6.4	313.4 15.3	12.25 0.6	3.69 0.13	35.42 1.1	174.9 4.6	179.3 5.3	126.4 4.7	183.9 5.3	150.6 3.16
BrO_3	6.38 0.38	36.67 2.2	152.5 8.20	0.59 0.025	0.30 0.009	0.8 0.02	30.0 0.9	85.17 2.3	42.86 1.5	58.43 1.8	1.3 0.03
IO_3	7.62 0.35	8.33 0.4	80.43 3.84	0.004 0.0_314	0.059 0.0_216	0.05 0.001	0.25 0.0_257	0.25 0.007	6.87 0.26	0.83 0.02	0.002 0.0_43
OH	142.9 18	116.4 21.	12.04 5.0	0.01 0.001	40.04 1.76	3.7 0.22	0.77 0.063	0.17 0.02	0.001 0.0_32	0.0_35 0.0_45	0.01 0.0_34
SO_4	11.11 0.62	16.83 1.15	35.64 2.8	0.55 0.020	4.74 0.09	0.0_323 0.0_410	0.011 0.0_36	0.20 0.015	35.43 2.8	53.12 3.1	0.0041 0.0_313
CrO_4	63.1 2.7	61.21 3.30	111.6 6.5	0.0025 0.0_315	0.006 0.0_31	0.0_338 0.0_415	0.12 0.006	0.4 0.03	73.0 4.3	. . . . . .	0.0_42 0.0_65
C_2O_4	30.27 1.6	3.34 0.24	7.22 0.69	0.0035 0.0_32	1.48 0.030	0.0086 0.0_338	0.0046 0.0_326	0.0_356 0.0_443	0.03 0.0027	0.0_36 0.0_44	0.0_315 0.0_55
CO_3	108.0 5.9	19.39 1.8	1.3 0.17	0.003 0.0_31	4.95 0.10	0.0023 0.0_311	0.0011 0.0_47	0.0013 0.0_313	0.1 0.01	0.004? 0.0_33?	0.0_31 0.0_43

The ***upper number*** in each square gives the number of grams of the anhydrous salt held in solution by 100 c.c. of water. The ***lower number*** is the molar solubility, *i.e.*, the number of moles contained in one liter of the saturated solution.

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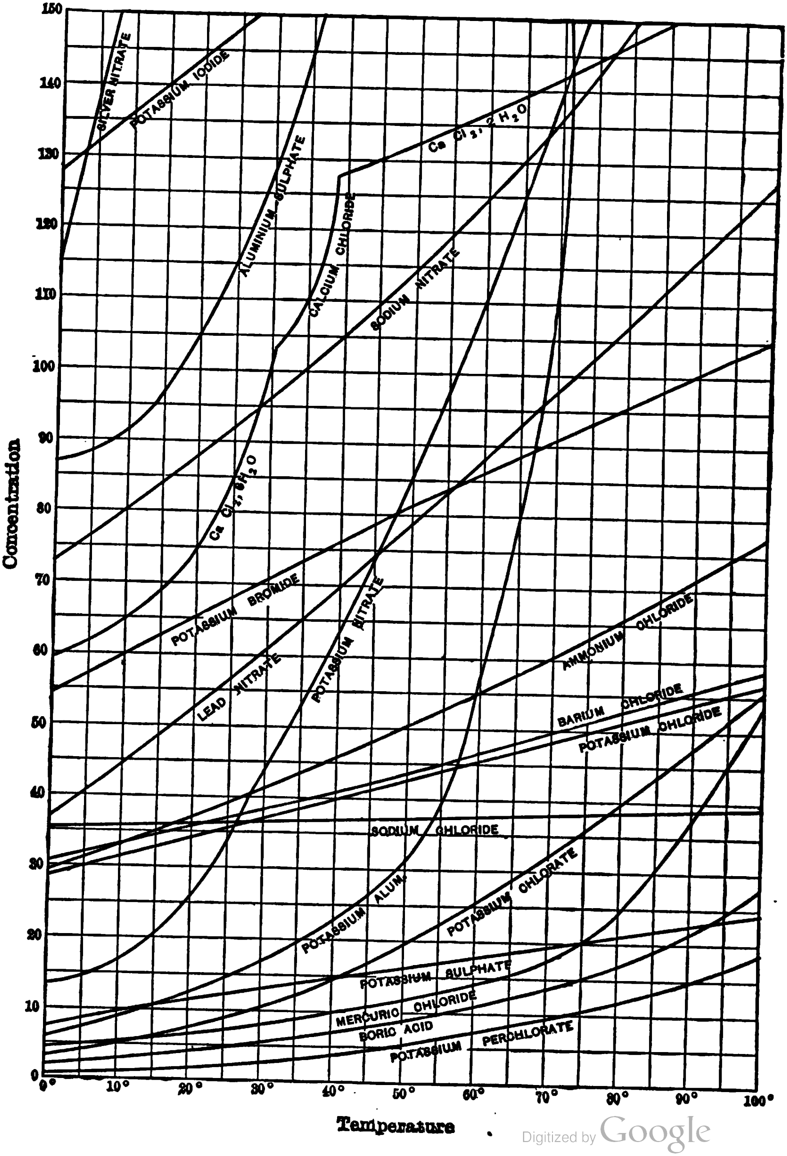

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VI. Degree of Ionization of Ionogens.

Except where otherwise specified, the figures give the fraction ionized in a normal, aqueous solution (usually at 18°). Subtraction of the figures from the unity gives the extent to which the ions will unite when brought together in normal concentration. At greater dilutions the ionization is greater and the union of ions less.

Acids.

HNO_3	0.82	$H.H_2PO_4$ (N/2)	0.17
HNO_3 (conc.)	0.09	$H.HC_2O_4$ (N/10)	0.50
HCl	0.78	$H.HC_4H_4O_6$ (N/10)	0.08
HCl (conc.)	0.13	$H.C_2H_3O_2$	0.0_24
HCl (N/2)	0.85	$H.C_2H_3O_2$ (N/10)	0.013
H_2SO_4	0.51	$H.HCO_3$ (N/10)	0.0_217
H_2SO_4 (conc.)	0.0_27	$H.HCO_3$ (N/25)	0.0_221
HBr (N/2)	0.90	H.HS (N/10)	0.0_37
HI (N/2)	0.90	$H.H_2BO_3$ (N/10)	0.0_81
$HClO_3$ (N/2)	0.88	HNC (N/10)	0.0_81
$HMnO_4$ (N/2)	0.93		

Bases.

KOH	0.77	$Sr(OH)_2$ (N/64)	0.93
NaOH	0.73	$Ba(OH)_2$ (N/64)	0.92
$Ba(OH)_2$	0.69	AgOH (N/1783)	0.39
NH_4OH	0.0_24	HOH	0.0_81
$Ca(OH)_2$ (N/64)	0.90		

Salts.

KCl	0.75	Na_2CO_3	0.40
KBr (N/32)	0.92	$Na.HCO_3$	0.52
$KClO_3$ (N/2)	0.79	$Na_2.HPO_4$ (N/32)	0.83
KNO_3	0.64	$NaC_2H_3O_2$	0.53
K_2SO_4	0.53	$Na_2C_4H_4O_6$ (N/32)	0.78
K_2CO_3	0.49	$BaCl_2$	0.57
$KMnO_4$ (N/32)	0.92	$CaSO_4$ (N/100)	0.63
$K_2Cr_2O_7$ (N/32)	0.94	$CuSO_4$	0.22
NH_4Cl	0.74	$AgNO_3$	0.58
NaCl	0.67	$CdSO_4$	0.22
Na_2SO_4	0.44	$ZnSO_4$	0.24
Na_2SO_3 (N/32)	0.82	$HgCl_2$	(<0.01)

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VII. Electromotive Series.

The electromotive force of a cell, in which each of the following metals constitutes in turn the negative pole (and gold, *e.g.*, the positive), diminishes in the order given. The tendency to enter the ionic condition in a solution already containing the same ion in normal concentration diminishes in the same order, and hence the ionic form of each of these metals (in normal concentration) is discharged and the metal liberated by every metal preceding it in the series.

Potassium	Cadmium	Arsenic
Sodium	Iron ($Fe^{\cdot\cdot}$)	Bismuth
Barium	Thallium	Antimony
Strontium	Cobalt	Mercury ($Hg^{\cdot\cdot}$)
Calcium	Nickel	Silver
Magnesium	Tin ($Sn^{\cdot\cdot}$)	Palladium
Aluminium	Lead	Platinum
Manganese	**Hydrogen**	Gold
Zinc	Copper ($Cu^{\cdot\cdot}$)	

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